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ON THE

PROGRESS OF CHEMISTRY

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Amer. Chem. J. . .	American Chemical Journal.
Amer. J. Physiol . .	American Journal of Physiology.
Amer. J. Sci. . . .	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim. anal. . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys. . .	Annales de Chimie et de Physique.
Ann. Physik . . .	Annalen der Physik.
Ann. Report . . .	Annual Reports of the Chemical Society.
Arch. expt. Path. Pharm. .	Archiv. für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim. . .	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Pharm. . . .	Archiv der Pharmazie.
Atti R. Accad. Lincei .	Atti della Reale Accademia dei Lincei.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Ber.	Berichte der Deutschen chemischen Gesellschaft
Ber. Deut. bot. Ges. . .	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. physikal. Ges. .	Berichte der Deutschen physikalischen Gesellschaft.
Bied. Zentr. . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. Bull. . . .	Biochemical Bulletin.
Bio-Chem. J. . . .	The Bio-Chemical Journal.
Biochem. Zeitsch. . .	Biochemische Zeitschrift.
Bull. Acad. roy. Belg. .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow .	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg	Bulletin de l'Academie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Soc. chim. . .	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par. . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min. . . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. News . . .	Chemical News.
Chem. Weekblad . .	Chemisch Weekblad.
Chem. Zeit. . . .	Chemiker Zeitung.
Chem. Zentr. . . .	Chemisches Zentralblatt.
Compt. rend. . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Deutsch. med. Wochensch. .	Deutsche medizinische Wochenschrift.
Gazzetta	Gazzetta chimica italiana.

* The year is not inserted in references to 1913.

Abbreviated Title.	Journal.
Intern. Sugar J.	International Sugar Journal.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. Phys.	Journal de Chimie physique.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Landw.	Journal für Landwirtschaft.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Koll. Chem. Beihefte	Kolloid-Chemische Beihefte.
Kolloid. Zeitsch.	Kolloid-Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Oesterr. Zeitsch. Berg.- u. Hüttenw.	Oesterreichische Zeitschrift für Berg.- und Hüttenwesen.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
P.	Proceedings of the Chemical Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. London Phys. Soc.	Proceedings of the London Physical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Univ. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Quart. J. expt. Physiol.	Quarterly Journal of experimental Physiology.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Archiv. Physiol.	Skandinavisches Archiv. für Physiologie.
T.	Transactions of the Chemical Society.
Trans. Eng. Ceram. Soc.	Transactions of the English Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.

Abbreviated Title.	Journal.
Zeitsch. Elektrochem. . .	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min. . .	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem. .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem. .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Photochem. .	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm. .	Zeitschrift für Zuckerindustrie in Böhmen.

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GENERAL AND PHYSICAL CHEMISTRY.

The past year has been characterised in the domain of Physical Chemistry by the publication of a large number of important papers, and many outstanding problems have been brought much nearer to solution. The method adopted in the present Report, as in past years, is to choose a few out of the many available topics, and to summarise the present position of knowledge of these subjects as fully as space permits.

Specific Heat of Solids.

The specific heats of a number of metals have been determined[1] with a high degree of accuracy at a series of temperatures between 0° and 100°. Great attention was paid to the purity of the metals; large quantities (1—3 kilos.) were used, and the temperature differences never amounted to more than 1·4°. The mean results are as follows, the first value in each case being for 0°, the second for 97·5°: copper, 0·09088, 0·09521; aluminium, 0·20957, 0·22482; iron, 0·10160, 0·1137; zinc, 0·09176, 0·09521; silver, 0·05560, 0·05737; cadmium, 0·05475, 0·05714; tin, 0·05363, 0·05690; lead, 0·03020, 0·03127. At 0° the relationship between the specific heat s and the atomic weight a is represented by the formula $s = 4{\cdot}804 \times a^{-0{\cdot}95}$.

Two entirely different methods for the determination of specific heats at high temperatures have been described. In the first,[2] a modified form of the Nernst copper block calorimeter was used. In order to diminish the loss of heat incurred in the introduction

[1] E. H. Griffiths and E. Griffiths, *Proc. Roy. Soc.*, 1913, A, **88**, 549; *A.*, ii, 753.

[2] A. Magnus, *Physikal. Zeitsch.*, 1913, **14**, 5; *A.*, ii, 103.

of the heated substance into the calorimeter, a block of copper 22 kilograms in weight was used, the rise of temperature being measured by means of 50 iron-constantan thermocouples, half the junctions being placed in deep holes in the block of copper, and the other half in the water-bath surrounding the Dewar vessel containing the copper block. The mean specific heats of a number of oxides and salts were measured between room temperature and 100°, 270°, 550°, and 750° respectively. In the other method,[3] an insulated, electrically heated tube furnace is used, the temperature of which is adjusted to that at which the specific heat measurement is to be made. Inside this is a much smaller tube furnace, the temperature of which is measured by means of a thermocouple. The relative amounts of electrical energy (measured by a watt-meter) required to raise the temperature of the inner furnace by the same definite increment when the tube is empty and when it is filled with the substance under experiment are determined, and from the data thus obtained the specific heat of the substance is calculated. Two other electrical methods somewhat similar in principle to the above are also described. The specific heats of tungsten and tantalum have been measured in this way at a series of temperatures between 350° and 1400°, and data are also recorded for iron between 160° and 970°. The curve representing the relationship between the specific heat, ρ, of iron and the temperature is very irregular, showing maxima at about 710° ($\rho = 0{\cdot}32$) and 850° ($\rho = 0{\cdot}26$), and a sharp minimum at about 790° ($\rho = 0{\cdot}20$). No decided change in any other physical property of iron at 790° has hitherto been observed.

The Einstein formula for the specific heat of a monatomic element[4] has been modified by Debye[5] on the assumption that a vibrating atom gives rise to a continuous spectrum corresponding with a continuous series of component vibrations, and the new formula is shown[6] to represent the experimental results more satisfactorily than either Einstein's formula or the modified form due to Nernst and Lindemann.

The available data for the specific heat show that two groups of elements have to be distinguished. In the one group the variation of the specific heat with temperature is satisfactorily represented by Debye's formula, whilst in the other group the diminution of specific heat with fall in temperature is less rapid

[3] M. von Pirani, *Ber. Deut. physikal. Ges.*, 1912, **14**, 1037; *A.*, ii, 102.

[4] *Ann. Report*, 1912, 6.

[5] P. Debye, *Ann. Physik*, 1912, [iv], **39**, 789; *A.*, 1912, ii, 1134.

[6] W. Nernst and F. A. Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 1100; *A.*, ii, 103.

than is required by the formula in question. It is suggested that crystalline elements belonging to the first group are monatomic, those belonging to the second group polyatomic.

Property-Composition Curves and their Interpretation: Theory of Binary Mixtures.

Few subjects have given rise to so much controversy as the interpretation of property-composition curves. In the case of binary mixtures of liquids, which have been most fully investigated from this point of view, the curve representing the variation of the physical property in question with the composition of the mixture usually belongs to one of three types; it may be a straight line or may be concave or convex with reference to the axis of composition. One view is that a curve approximating to a straight line indicates little or no action between the components, whereas a concave or convex type indicates alteration in the degree of association or chemical combination of the components. According to the school of van der Waals, on the other hand, the phenomena in question are due mainly to molecular attraction, which may or may not be accompanied by chemical combination, but one is not entitled to interpret deviations from a straight line as necessarily indicating either chemical combination or change in the degree of association. These two points of view are illustrated in the present section dealing with vapour-pressure curves, and in the next two sections on viscosity, and on other properties of binary mixtures.

Some years ago a theory of binary mixtures and concentrated solutions based on the results of vapour-pressure measurements was put forward by Dolezalek,[7] and has led to results of considerable importance. According to this theory, the regular form of the total pressure-composition curve is a straight line, and the apparent exceptions occur (1) when one or both of the components is complex, the curve being then concave to the axis of composition; (2) when the components enter into chemical combination, the curve being then convex towards the axis of composition. The composition of the mixture is expressed as the relative number of mols. of each component present, and the essential feature of the theory is that the partial pressure of each component of the mixture is equal to the saturation pressure of the pure component multiplied by the molecular fraction of this component in the liquid mixture. On this basis comparatively simple formulæ have been derived, which give the relationship between the partial and total pressures and the constant for the equilibrium between simple

[7] F. Dolezalek, *Zeitsch. physikal. Chem.*, 1908, **64**, 627; 1910, **71**, 191; with A. Schulze, 1913, **83**, 40; *A.*, 1909, ii, 22; 1910, ii, 184; 1913, ii, 481.

and complex molecules, or between a chemical compound and its components. These equations therefore admit of the determination of the constitution of mixtures and also of pure liquids, and it is contended that this is the only method for determining the molecular complexity of liquids which has a satisfactory theoretical basis.

It may rightly be objected that the theory in question is rather arbitrary, inasmuch as it is based on the assumption that the gas laws apply to the most concentrated solutions, and the considerable deviations are ascribed to association or chemical combination, the amount of association or combination assumed being just sufficient to bring the behaviour of the mixture into conformity with the simple laws. It is clear that some independent method of controlling the deductions from the theory is necessary. This has been secured in a recent investigation[8] on binary mixtures of ethyl ether and chloroform, and the concordance of the results obtained by different methods lend considerable support to the theory.

The vapour pressure-composition curve of the system ethyl ether–chloroform is convex to the axis of composition at low temperatures, and approximates to a straight line as the temperature is raised. The theory in question leads to the conclusion that a compound of one molecule of each component exists in the mixture in equilibrium with its components according to the law of mass action, and that this compound dissociates progressively with rise of temperature. The existence of this compound has been independently confirmed: (1) by isolating it in the solid state, it freezes at $-80°$, about 30° above the melting point of ether; (2) from the observation that on mixing the vapours of ether and chloroform at 80° a contraction occurs which is not due to the deviation of the vapours from the gas laws. Further confirmation of these conclusions is afforded by the fact that heat is given out on mixing ether and chloroform, and that both the viscosity and the density of the binary mixture deviate from the mixture rule.

The above theory has been criticised by van Laar,[9] who ascribes the deviations from the mixture rule in binary systems to molecular attraction, on the lines of van der Waals' theory. It is pointed out that the components will only be without influence on each other when (on certain assumptions as to the magnitude of the molecular attraction) the critical pressures of the components are equal. Dolezalek, in his reply, points out that the vapour pressure-composition curve of benzene–ethylene dichloride is a straight line,

[8] F. Dolezalek and A. Schulze, *loc. cit.*

[9] J. J. van Laar, *Zeitsch. physikal. Chem.*, 1910, **72**, 723; 1913, **83**, 599; *A.*, 1910, ii, 583; 1913, ii, 670.

although their critical pressures are 48 and 53 atmospheres respectively, and maintains that the fact that the property-composition curves of many binary mixtures which show deviations at low temperatures approach a straight line at high temperatures is alone sufficient to disprove van Laar's views. In spite of the interesting results obtained by Dolezalek, it appears to the writer that there is much force in van Laar's objections. It does not appear justifiable to postulate, as Dolezalek does, that the property-composition curve is necessarily a straight line when no chemical combination or association occurs, and the last argument, based on the approximation to the mixture law with rise of temperature, is far from convincing. The question at issue is of fundamental importance for the theory of solution.

Measurement of Viscosity: The Viscosity of Binary Mixtures.

The number of workers devoting themselves to the study of the viscosity of liquids continues to increase, and some important problems in this field appear to be approaching solution. A specially gratifying feature is the greater attention now being paid to the attainment of a high degree of accuracy in the measurements. In this connexion the names of Bingham and of Hartley and their co-workers deserve special mention. The corrections to be applied to measurements with the Ostwald viscometer have been fully discussed.[10] An improved form of the Ostwald viscometer, constructed of quartz, has been described; among other advantages possessed by this instrument, its dimensions do not change appreciably with temperature.[11] A special form of viscometer for use with volatile liquids has been devised.[12]

Many attempts have been made to express the viscosity as a function of the temperature, but without success. It is now shown[13] that viscosity is a function of the specific volume. The expression $\eta = c/(v-w)$ has been deduced, where v represents the specific volume, and c and w are constants characteristic of any particular liquid, and on the basis of the extensive data of Thorpe and Rodger is shown to hold for all non-associated liquids over wide limits of variation of the co-ordinates; with ethyl acetate, for example, over a temperature-interval exceeding 180°. The law is

[10] E. C. Bingham, *T.*, 1913, **103**, 959; M. P. Applebey, *ibid.*, 2167.

[11] E. W. Washburn and G. Y. Williams, *J. Amer. Chem. Soc.*, 1913, **35**, 737; *A.*, ii, 557.

[12] J. P. Kuenen and S. W. Visser, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 75; *A.*, ii, 833.

[13] A. J. Batschinski, *Ann. Soc. d'Encour. Sci. Exp. Supp.* 3, 1913, i; *Physikal. Zeitsch.*, 1912, **13**, 1157; *A.*, ii, 26, 928.

not applicable to associated liquids, but in the case of very dense gases seems to be followed to the same extent as with liquids. The relationship between the constant w and other properties of the liquid is discussed.

As regards the viscosity of binary mixtures of liquids, a great deal of attention is still being devoted to the interpretation of the maxima and minima on the curves representing the variation of viscosity with composition. The original explanation of Graham that the maxima in question correspond with the formation of definite compounds has found supporters until quite recently, but is no longer regarded as generally applicable.[14] That is does apply in certain cases[15] has recently been shown very strikingly by the investigation of certain binary systems containing a thiocarbimide and an organic base which form definite compounds, and at the same time remain liquid and homogeneous. The viscosity isotherms of these systems consist of two separate branches, which are convex to the composition axis and intersect at an angle (increasing in acuteness as the temperature is lowered) in a maximum corresponding with equimolecular proportions of the components. Such results, however, are only obtained when chemical combination is practically complete; when such is not the case, the position of the maximum is no evidence of the composition of the compound. In fact, the important matter in this connexion is not the position of the maximum, but the position of greatest deviation from the mixture law.[16] That these may differ considerably is shown by the fact that the maximum on the viscosity curve of the system pyridine–water at 25° occurs at a composition of 32 per cent. of pyridine, whereas the maximum deviation from a straight line occurs at 68 per cent. of pyridine, corresponding with the compound $C_5H_5N,2H_2O$. It is stated[17] that change of temperature does not alter the position of a maximum on the deviation curve, and that the deviation from a straight line is a maximum for the composition corresponding with that in the compound. These important statements deserve further investigation on the basis of more extensive data. The main results of the viscosity measurements with binary mixtures with special reference to the interpretation of maxima and minima on the curves, have recently been discussed by Dunstan and Thole,[18] to whom we owe a large number of useful papers on this subject.

[14] Compare E. C. Bingham, G. F. White, A. Thomas, and J. L. Cadwell, *Zeitsch. physikal. Chem.*, 1913, **83**, 641; *A*, ii, 675.

[15] N. S. Kurnakov and S. F. Shemtschushni, *ibid.*, 481; *A.*, ii, 1910.

[16] A. Findlay, *ibid.*, 1909, **69**, 203; *A.*, 1909, ii, 975; R. B. Denison, *Trans. Faraday Soc.*, 1912, **8**, 20; *A.*, ii, 30.

[17] Denison, *loc. cit.*

[18] A. E. Dunstan and F. B. Thole, *T.*, 1913, **103**, 1108.

Summarising the results of recent investigations, it would probably now be agreed that owing to insufficient appreciation of the factors concerned, too much stress has been laid on the position of maxima on viscosity composition curves, and, further, that the absence of a maximum on a curve does not necessarily indicate the absence of chemical combination. A further point, to which sufficient attention has not been directed, is whether the additive character is most pronounced for viscosities or for the fluidities, the reciprocals of the viscosities. It is contended by Bingham [19] that when the results are not complicated by association or dissociation the fluidities are strictly additive, but this view implies an assumption the uncertainty of which has already been referred to in another connexion (p. 5).

Other Properties of Binary Mixtures of Liquids.

The solubility of hydrogen, oxygen, and nitrogen has been determined [20] in aqueous solutions of sucrose, dextrose, glycerol, and chloral hydrate, varying in concentration from 10 to 60 per cent. In the glycerol and chloral hydrate solutions the absorption coefficient decreases to a minimum, and then increases with increasing concentration of the solutions, whilst in the sucrose and dextrose solutions the absorption coefficient diminishes steadily with increasing concentration. The relative decrease in the absorption coefficient at a given concentration of the solution is independent of the nature of the gas in the cases examined. The minimum absorption occurs at about the same concentration, 50—60 per cent. for both glycerol and chloral hydrate, for all the gases examined. The results show clearly that such substances as chloral hydrate and glycerol in solution have considerable solvent power for gases. In the opinion of the author, the occurrence of minima independent of the nature of the gas point to the existence of hydrates in solution, but the method of calculating the degree of hydration in solution on the assumption that the hydrated solute has no solvent power for gases is not valid. Similar minima in solubility curves of gases are met with in the case of binary mixtures of ethyl alcohol and water and of sulphuric acid and water (Setchenow, 1876). In the former case the minima occur in mixtures containing about 30 per cent. of alcohol. In this connexion it is interesting to note [21] that when the heat of solution of the chlorides and nitrates of sodium and potassium in water–ethyl

[19] *T.*, 1913, **103**, 964.
[20] C. Müller, *Zeitsch. physikal. Chem.*, 1912, **81**, 483 ; *A.*, ii, 30.
[21] N. de Kolosovski, *ibid.*, 713 ; **83**, 79 ; *A.*, ii, 308, 671, 672.

alcohol mixtures is determined, the maximum absorption occurs in the mixture containing 33 per cent. of alcohol, which approximately corresponds with the mixture of alcohol and water giving the maximum heat of solution. The greatest deviation of the fluidity curve from a straight line occurs, however, in mixtures containing 44—51 volume per cent. of alcohol[22] at 25°. This is a fair sample of the contradictory results met with in attempts to determine the composition of solvates in solution. It has been recognised for many years that many dissolved substances are combined to a greater or less extent with the solvent, but we appear to be as far as ever from any definite knowledge of the degree of solvation (hydration) in any given case.

Effect of Pressure on Physical and Chemical Change.

An important paper[23] from the Geophysical Laboratory at Washington deals with the effect of high pressure on the physical and chemical behaviour of solids. It is pointed out that in this connexion it is necessary to distinguish between the effects of uniform pressure and of non-uniform pressure. The effects produced by non-uniform compression are generally permanent; that is, the original state of the system is not re-established when the pressure is released. Most of the work on the influence of high pressures on solids has been carried out under these conditions, and it seems probable that many of the apparently contradictory statements recorded in the literature are due to the disregard of the distinction between the two types of compression.

Uniform pressure usually raises the melting point, and by an amount which seldom exceeds 10° and is never greater than 30° per 1000 atmospheres in any system hitherto investigated; its effect on solubility is also slight. Non-uniform pressure, on the other hand, always lowers the melting point and increases the solubility, and by amounts which are many times greater than the corresponding changes with uniform pressure. The actual cause of the phenomena recorded as occurring when solid systems are subjected to compression is supposed to be the local melting produced by non-uniform compression, and on the assumption that permanent deformation of a crystalline aggregate is always conditioned by such liquefaction it is found that the pressure required to produce this change at the ordinary temperature is well within the bounds of probability.

From an examination of the available data, especially of the results obtained by Spring, the authors draw a number of con-

[22] Bingham, White, Thomas and Cadwell, *loc. cit.*

[23] J. Johnston and L. H. Adams, *Amer. J. Sci.*, 1913, [iv], **35**, 205 ; *A.*, ii, 290.

clusions with respect to the physical and chemical behaviour of solids under high pressures.

The amount of compression required to cause crystalline solids to "flow" or to weld together is dependent mainly on the melting point, the heat of fusion, and density of the substance and the temperature of experiment; therefore the substances with the highest melting points are usually those which require the highest temperature to weld them.

Compression alone will not in general cause crystallisation of a material or the transformation of one form into another. If, however, the velocity of transformation is appreciable, it will do so in certain cases, and if, further, the conditions are such that partial liquefaction occurs, compression will cause a partial transformation.

With reference also to chemical reactions between solids, non-uniform pressure has a much greater effect than uniform pressure. The reaction under uniform pressure takes place only at the surfaces of contact, and hence only a small total amount of a compound is formed, but if the compression is not uniform there is a renewal of the surfaces which allows the reaction to proceed further. This renewal may also be advanced by a flowing away of the reaction product if its melting pressure is attained. Several of the criteria used by Spring to determine the condition of compressed systems are altogether insufficient; for example, the condition of equilibrium in the solid state of the system $BaSO_4 + Na_2CO_3 \rightleftarrows Na_2SO_4 + BaCO_3$ is quite unknown.

The results of an extensive investigation[24] on the pressure and hardness of plastic substances have recently been published. Under slow deformation the substances behave like liquids of high viscosity, and under rapid deformation like brittle, elastic solids. It is shown that when the pressures on the piston from which flow takes place are plotted as ordinates against the times as abscissæ four principal types of curve are obtained, and these types are discussed in detail. The hardness number and the pressure of flow may serve as characteristics of the purity of metals.

An apparatus has been devised[25] for direct visual observation of the influence of pressure on the critical solution temperature of binary mixtures of liquids up to pressures of about 3000 atmospheres. The results are in accord with theoretical predictions throughout. The system water–methyl ethyl ketone is of particular

[24] N. S. Kurnakov and S. F. Shemtschushni, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1004; *A.*, ii, 929.

[25] P. Kohnstamm and J. Timmermans, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1021; *A.*, ii, 481.

interest, inasmuch as it can be converted from a partly miscible to a completely miscible condition by change of pressure at constant temperature.

Within the last few years a series of very accurate observations on the effect of high pressures on various chemical and electrochemical changes have been carried out in the Utrecht laboratory by E. Cohen and his co-workers. The effect of change of pressure on the *E.M.F.* of cells determined experimentally has been found to agree fairly well with the values calculated from the change of volume of the system.[26]

In a recent investigation[27] on the influence of high pressures on Faraday's first law, the relative amounts of silver deposited in two coulometers, one at atmospheric pressure and the other at pressures of 500, 1000, and 1500 atmospheres, were found to be identical within the limits of experimental error. From these results the conclusion is drawn that the ionic charge varies less than 1 in 17,000 on changing the pressure from 1 to 1500 atmospheres.

The effect of pressure on the rate of hydrolysis of sucrose[28] in the presence of dilute hydrochloric acid has been determined. After correcting for the change in concentration of the sugar owing to the slight compressibility of the solution, the reaction velocity is found to have decreased by 8 per cent. at a pressure of 500 atmospheres, by 19 per cent. at 1000 atmospheres, and 26 per cent. at 1500 atmospheres. It has been stated[28a] that in some cases pressure accelerates, in other cases retards, the inversion of sugar, depending on the nature of the acid, and this point is being further investigated.

Finally, with reference to the influence of pressure on solubility[29] at 24·05° and atmospheric pressure, 35·90 grams and, at 1500 atmospheres, 37·36 grams of sodium chloride are dissolved by 100 grams of water, whilst at the same temperature 20·66 and 21·64 grams of mannitol are dissolved at 1 and 1500 atmospheres respectively.

Dynamic Allotropy: Polymorphism.

The new theory of dynamic allotropy put forward by Smits, briefly referred to in a previous report,[30] has excited considerable

[26] *Zeitsch. physikal. Chem.*, 1910, **75**, 219; *A.*, 1910, ii, 1029; *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 161; *A.*, ii, 823.

[27] E. Cohen, *Zeitsch. Elektrochem.*, 1913, **19**, 132; *A.*, ii, 181.

[28] E. Cohen and R. B. de Boer, *Zeitsch. physikal. Chem.*, 1913, **84**, 41; *A.*, ii, 687.

[28a] Dammer, *Handbuch der anorg. Chem.*, 1903, Vol. IV, p. 73.

[29] E. Cohen, K. Inouye, and C. Euwen, *Zeitsch. physikal. Chem.*, 1910, **75**, 257; *A.*, 1911, ii, 23.

[30] *Ann. Report*, 1911, 21.

attention during the last three years. So-called dynamic allotropy, in which the different allotropes can exist in equilibrium through a wide range of temperature, has been known for some time in the case of liquids, for example, fused sulphur. The essential feature of Smits' theory is that such equilibria exist also within the solid allotropic modifications. Each phase therefore consists of mixed crystals of the two components in equilibrium, the relative proportions of the components being different in the two phases. The transition temperature represents the point at which the crystalline modifications cease to be completely miscible. According to this view, the temperature at which miscibility ceases is in the case of enantiotropy below, and in the case of monotropy above, the stable unary melting point. The theory should, strictly speaking, be termed dynamic isomerism, as it applies to chemical compounds as well as to elements.

In support of this view, the behaviour of the different modifications of sulphur, of phosphorus, and especially of mercuric iodide, is cited.[30a] The transition temperature between the red and the yellow phase of the compound last mentioned lies at 127°. If now the yellow modification is heated for some time at 210°, and then suddenly cooled to 130° (which is slightly above the transition point), particles of the red phase are momentarily observed, but disappear after a few seconds. It is suggested that owing to the sudden cooling the equilibrium within the phase does not adjust itself at once, and therefore the presence of the red modification is indicated by its momentary appearance. It may be said at once that in a recent investigation of this point in Tammann's laboratory,[31] the above statements regarding the behaviour of mercuric iodide could not be confirmed. Similarly, the statement that the melting point of colourless phosphorus is altered by heating to 100° and cooling rapidly, a result also cited in favour of the new theory of allotropy has not been confirmed by other observers.[32] The new theory has been applied to explain Ostwald's law of transition by steps in connexion with the appearance of new phases,[33] and also to the discussion of equilibria in the systems sulphur [34] and silicon dioxide.[35]

The new theory of allotropy has been severely criticised by

[30a] *Zeitsch. physikal. Chem.*, 1911, **76**, 421; 1913, **84**, 250; *A.*, 1910, ii, 195, 400; 1913, ii, 393.

[31] M. Hasselblatt, *ibid.*, 1913, **86**, 61.

[32] A. Stock and E. Stamm, *Ber.*, 1913, **46**, 3497; *A.*, ii, 1051.

[33] A. Smits, *Zeitsch. physikal. Chem.*, 1913, **84**, 385; *A.*, ii, 933.

[34] A. Smits, *ibid.*, 1913, **83**, 221; *A.*, ii, 499.

[35] A. Smits and K. Endell, *Zeitsch. anorg. Chem.*, 1913, **80**, 176; *A.*, ii, 318.

Tammann,[36] mainly on the ground that it is merely an only partly successful attempt to represent graphically the changes of concentration within the different phases attending the crystallisation of associated liquids, and that it does not fulfil one of the main purposes of a theory, that of correlating different groups of facts. He himself puts forward an atomistic theory of polymorphism,[37] based on the experimental fact that for non-associated liquids only one crystal group separates, whilst for associated liquids more than one crystal group may separate. According to his view, polymorphism is due to different arrangements of the molecules, and the essential feature of the transformation of one phase to another is the arrangement in another space lattice.

Benedicts, [38] on the other hand, expresses views on polymorphism similar in some respects to those of Smits. An allotropic change is not necessarily a sudden transformation of one form into another, since there is always the possibility that one or both forms may have a certain solubility in the other. This is shown to apply in the case of silver iodide, the regular modification stable above the transition temperature, 147°, being soluble to some extent in the hexagonal modification. The transformation point, A_3, of iron at about 890° is of the same type, and this leads to the conclusion that the so-called β-iron is really α-iron containing in solution a limited amount of γ-iron, increasing with the temperature.

The study of the different forms of sulphur and of phosphorus has been prosecuted by a number of workers, but many problems yet remain unsolved. A third variety of sulphur,[39] differing from S_λ and S_μ, has been separated from the product obtained by the rapid cooling of sulphur which has been heated at 165—170°. This modification, which has been termed S_π, may be identical with the "crumbly sulphur" described by Magnus (1856).

Experimental details as to the allotropic modifications of these and other elements belong more properly to the section on Inorganic Chemistry, and will therefore not be further considered here.

Osmotic Pressure.

A new and very convenient method [40] for the direct determination

[36] G. Tammann, *Zeitsch. physikal. Chem.*, 1913, **82**, 172; **84**, 753; *A.*, ii, 193, 679.

[37] *loc. cit.*

[38] C. Benedicts, *8th. Inter. Cong. Appl. Chem.*, 1912, **22**, 13; *A.*, ii, 752; *J. Iron Steel Inst.*, 1912, **86**, 242; *A.*, ii, 599.

[39] A. H. W. Aten, *Zeitsch. physikal. Chem.*, 1912, **81**, 257; 1913, **83**, 442; **86**, 1; *A.*, 1912, ii, 40; 1913, ii, 580.

[40] E. Cohen and G. de Bruin, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 160; *A.*, ii, 838.

of osmotic pressure has recently been described. A porous pot holding a semi-permeable membrane is filled with the solution to be examined, and closed by a stopper, through which passes a capillary tube and a copper wire supporting a copper electrode. A second copper electrode is placed in the surrounding water vessel. The porous pot is then immersed in the water, and the liquid immediately begins to rise in the capillary. An *E.M.F.* just sufficient to prevent the liquid rising any further is then applied to the electrodes, and the height of the liquid in the capillary measured. If h_1 represents the height of the liquid in the capillary, E_1 the counterbalancing *E.M.F.*, and P the osmotic pressure, then $P-h_1=kE_1$, where k is a constant. If on breaking the circuit the liquid again rises, say, to h_2, and the counterbalancing *E.M.F.* is E_2, then $P-h_2=kE_2$, and

$$P=h_1+(h_1-h_2)E_1/(E_2-E_1).$$

The advantages of the method are (1) the short time required for making an experiment, (2) the durability of the membrane, since it has a pressure on both sides, (3) the absence of volume change of solution by entrance of solvent.

The Hydrolysis of Sucrose: The Nature of Hydrolysis.

The latest instalment of the important investigations of Armstrong and his colleagues[41] on the nature of solutions belong more particularly to the section on catalysis, but it is convenient to consider them separately.

Some years ago it was stated by E. F. Armstrong and Caldwell[42] that in its initial stages the velocity of hydrolysis of sucrose in the presence of dilute acids is a linear reaction, independent of the concentration of the sucrose. This announcement was all the more interesting in view of the well-known fact that the hydrolysis of sucrose by invertase is a linear reaction within certain limits of concentration of the sucrose solution. It has now been shown in two independent series of investigations[43] that the hydrolysis of sucrose in the presence of dilute acids is a unimolecular reaction in accordance with the law of mass action, and that the results obtained by Armstrong and Caldwell were probably due to an error in the initial reading of the polarimeter. Worley, who in the course of the investigations designed to settle the point just

[41] H. E. Armstrong with E. E. Walker and F. P. Worley, *Proc. Roy. Soc.*, 1912, A, **87**, 539; *A.*, ii, 117.

[42] E. F. Armstrong and R. J. Caldwell, *ibid.*, 1904, **74**, 195; *A.*, 1904, i, 1070.

[43] M. A. Rosanoff, R. H. Clark and R. L. Sibley, *J. Amer. Chem. Soc.*, 1911, **33**, 1911; *A.*, 1912, ii, 34. F. P. Worley, *loc. cit.*, p. 555; *A.*, ii, 117.

referred to has brought the measurement of hydrolysis based on polarimetric observations to a high degree of accuracy, has also investigated the hydrolysis of sucrose in the presence of sulphuric acid. On comparing the final negative rotation at the completion of hydrolysis with the initial positive rotation of the sucrose, it was found that this ratio decreased very considerably as the dilution was increased, the variation being from 0·342 for the most concentrated solution to 0·298 for the most dilute. As the ratio of sugar to acid was the same in most of the experiments, it is not possible to say definitely how much of the variation is due to the variation in the concentration of the sugar, and how much to that of the acid, but it is probable that the lævulose is responsible for the greater part of the effect. In view of this phenomenon and of the mutarotation of the dextrose and lævulose, it might be doubted whether the polarimetric method affords a satisfactory measure of the rate of hydrolysis of sucrose. The author shows, however, from a theoretical discussion of the subject, that the velocity coefficient is not affected either by an alteration in the rotatory power of the invert sugar as a consequence of the presence of the acid or by the mutarotation of the hexoses. In a later paper[44] it is shown that the large alteration produced by benzenesulphonic acid in the value of the ratio of the final to the initial rotation can be explained by the changes produced by the acid on the rotatory powers of the three sugars involved. These investigations show how much care is necessary in order to obtain satisfactory measurements of the speed of reaction by the polarimetric method. The same author has investigated the rate of hydrolysis of methyl acetate in the presence of hydrochloric acid with and without the addition of neutral salts in order to obtain values of the "apparent molecular hydration" of the acid and salts employed. The molecular hydration values thus obtained are much smaller than the corresponding numbers obtained when sucrose and raffinose are used as hydrolytes, and it is considered probable that the differences in question represent actual differences in the condition of the acid in the presence of such different hydrolytes as methyl acetate and sucrose.

In the last paper of this instalment H. E. Armstrong and Worley[45] discuss the nature of the hydrolytic process in the light of the experimental results obtained in this series of papers, and suggest a qualitative explanation on the lines fully described in previous reports. According to this view, hydrolysis is essentially an associative process, which involves the association and direct

[44] F. P. Worley, *Proc. Roy. Soc.*, 1913, A, **88**, 439 ; *A.*, ii, 652.
[45] *loc. cit.*, p. 604.

interaction of two complexes, one of which consists of the hydrated hydrolyte and the other of the hydrated catalyst. Such associated systems are being constantly produced, broken down, and re-formed in such a way that whilst some give rise to the original components, others give rise to the products of change. The increase of molecular conductivity to a maximum on dilution is attributed partly to a gradual increase in the extent of the interaction between the solute and water, and partly to the gradual simplification of the complexes formed by the dissolved substance. On the other hand, the decrease of molecular chemical activity, as exemplified by the hydrolytic activity of the acids, to a minimum on dilution is regarded as the necessary result of the gradual weakening of the acid by further combination with water. The greater the extent to which the acid is used up in combining with water the less must be the residual activity available for hydrolytic processes.

In conclusion, the more important advances in knowledge resulting from these investigations are summarised. In the first place, it is claimed that an advance in the method of studying the properties of solutions was made in Part I by referring the concentration of substances in solution to a given mass of solvent instead of a given volume of solution. "Throughout the inquiry, volume has been disregarded in making up solutions, the relative molecular proportions of the dissolved substance to a given quantity of solvent being alone considered." The only drawback to this method, according to the authors, is that the amount of water actually free to act as such is subject to variation owing to the fact that part of it is combined with the substances present in solution. It appears to the writer that although the new method of making up solutions, which was put forward by Morse and Frazer some years ago on the basis of osmotic pressure measurements, has considerable advantages, it has one serious disadvantage from the point of view of the kinetic theory. Taking, for example, a bimolecular reaction as assumed by the authors for the hydrolysis of sucrose, the mean free path of the reacting molecules depends on the total volume, and therefore, other things being equal, the number of collisions and therefore the velocity of reaction must depend on the total volume. It is true that this effect will be difficult to disentangle from the many other effects produced by the addition of various substances to a solution, but it should not for that reason be overlooked.

A second point is the determination of the extent to which salts are hydrated in solution, one of the main objects of the inquiry. The method first adopted involved merely the determination of the number of molecular proportions of water that were necessary to reduce the rate of change in presence of a molecular

proportion of the salt to that obtaining in the presence of the acid catalyst alone,[46] but it is now recognised that "the numbers thus obtained do not necessarily represent the actual degree of hydration of the salts, but are rather a measure of the sum of the changes effected in the solution by their presence."

A new, or rather a modified, theory of sugar hydrolysis has recently been put forward by Rosanoff and Potter.[47]

Catalysis.

At the present time an increasing number of workers are devoting their attention to the mechanism of chemical reactions in general, and more particularly to those usually termed catalytic actions.[48] It is now usual to apply the term catalytic to any reaction the velocity of which is altered by the addition of a substance which does not enter into the equation representing the initial and final products of the reaction. According as the velocity is increased or diminished by the addition of the catalyst, we speak of positive or of negative catalysis. It should perhaps be noted that the fundamental question as to whether a catalyst may start a reaction or whether its action is confined to altering the velocity of a reaction which can proceed in the absence of a catalyst, still awaits definite decision.

The main result of recent investigation in this branch of physical chemistry is to strengthen the validity of the explanation of most catalytic actions as being connected with the formation of intermediate compounds. An excellent example of this, described briefly in last year's report,[49] is the proof adduced by Goldschmidt, Bredig, and their colleagues that ester formation in the presence of acids in alcoholic solution proceeds through the intermediate formation of complexes between the alcohol and the $H^{\cdot}$ and non-ionised acid respectively. The latter point, that both $H^{\cdot}$ and the non-ionised acid exert a catalytic effect in ester formation is an illustration of an important principle, to which attention was directed almost simultaneously by several investigators[50] that in many chemical reactions both non-ionised substances and their products of ionisation take part in the change. This statement applies to the catalyst

[46] R. J. Caldwell, *Proc. Roy. Soc.*, 1906, A, **78**, 272; *A.*, 1907, ii, 14; H. E. Armstrong and R. J. Caldwell, *ibid.*, 1907, A, **79**, 586; *A.*, 1907, ii, 850.

[47] M. A. Rosanoff and H. M. Potter, *J. Amer. Chem. Soc.*, 1913, **35**, 248.

[48] An excellent review of recent progress in catalysis is given by E. Abel, *Zeitsch. Elektrochem.*, 1913, **19**, 933.

[49] *Ann. Report*, 1912, 24.

[50] G. Senter, *T.*, 1907, **91**, 460; S. F. Acree and S. Nirdlinger, *Amer. Chem., J.*, 1907, **38**, 489; *A.*, 1907, ii, 857; A. Lapworth, *T.*, 1908, **93**, 2197.

as well as to the substance acted on. It should be pointed out that the above views in the special case of hydrogen chloride acting as catalyst appear to have been first definitely expressed by Lapworth [51] in connexion with his work on the effect of water on the activity of acids in alcoholic solution, and were later independently formulated by Goldschmidt and extended by Bredig on the basis of extensive experimental data. Within the last few years Acree [52] and his co-workers have also published a number of important papers on this subject, in which particular attention has been devoted to the relative activities of non-ionised molecules and their products of ionisation. In some of the reactions investigated by them there is considerable difference of opinion as to the interpretation of the experimental data.[53]

The recent results in two or three special sections of catalysis will now be briefly considered.

Neutral Salt Action.—Recent work on the elucidation of the fact that neutral salts increase the catalytic activity of acids, and in certain cases also of alkalis, has naturally been influenced by the suggestion of Snethlage [54] that the increased activity is due to the greater catalytic action of the undissociated molecule as compared with the $H^{\cdot}$ ion when strong acids are concerned.[54a] That this suggestion can be regarded as a complete explanation of the results is scarcely probable in view of Walden's work [55] on the increase in the ionising power of solvents caused by addition of salts. Moreover, the fact that the rate of change of neutral salt action with the nature of the acid is so different in the case of the inversion of sucrose and of ester catalysis [56] is difficult to reconcile with Snethlage's hypothesis.

Further data on neutral salt action have been accumulated at the Nobel Institute, but so far no general conclusions have been drawn from the results. It is shown [56a] that, contrary to the contention of Lundén,[57] the neutral salt effect is not independent of the concentration of the catalysing acid, since with increasing dilution of hydrochloric acid (used as catalyst in the hydrolysis of esters) from 0·5 to 0·01*N* the neutral salt effect progressively increases

[51] *Loc. cit.*

[52] For summary of work see S. F. Acree, *Amer. Chem. J.*, 1913, **49**, 345.

[53] Compare A. Michael, *ibid.*, 1910, **43**, 322 ; *A.*, 1910, i. 341.

[54] *Ann. Report*, 1912, 25.

[54a] The paper by Dawson and Powis on the relative catalytic activities of $H^{\cdot}$ and the undissociated acid (*T.*, 1913, **103**, 2135) appeared too late to be considered in the present report.

[55] This Report, p. 23.

[56] H. S. Taylor, *Medd. K. Vetensk. Nobelinst*, 1913, **2**, No. 35 ; *A.*, ii, 940, 941.

[56a] H. S. Taylor, *loc. cit.*, p. 8.

[57] H. Lundén, *Medd. K. Vetensk. Nobelinst*, 1911, **2**, No. 3, 1 ; *A.*, 1912, ii, 148.

from about 41 to 55 per cent. Further investigations on the effect of neutral salts on the activity of acids towards methyl-orange have also been carried out.[58]

Negative Catalysis.—Additional evidence in favour of the view that negative catalysis is to be ascribed to the action of the catalyst in diminishing the concentration of one or more of the substances taking part in the action[59] has been obtained in the course of an investigation on the effect of strong acids on the rate of reaction between water and halogen substituted acids. It is shown that the formulæ usually employed to represent negative catalysis are not valid, and the mathematical formulation of this phenomenon is discussed.

Influence of the Catalyst on the Equilibrium.—It was formerly widely accepted, on the basis both of experiment and of theoretical considerations, that the catalyst has no effect on the position of equilibrium in a reversible reaction. It has now been shown, however, that this view is erroneous, most convincingly, perhaps, from an investigation of the equilibrium between ethyl acetate, water, and its products of hydrolysis.[59a] Thus when the ratio of the amount of water to the amount of hydrogen chloride falls, the equilibrium constant $\kappa = [\text{ester}][\text{water}]/[\text{alcohol}][\text{acid}]$ rises from 4 to at least 8. The authors interpret their results on the basis of combination between the acid and water.

Colloids.

During the past year very important advances have been made in our knowledge of colloidal systems, but only a few of the publications on the subject can be considered here.

From the results of an investigation[60] of the electrical synthesis of colloids by Svedberg's method it appears that the disintegration process is essentially thermochemical. When the arc discharge takes place intermittently it is found that the surfaces of the electrodes show well-marked eruptive craters which are attributed to the melting of the metal under the influence of the discharge. When the discharge ceases, the hot metal comes into contact with the surrounding liquid, and disintegration follows. On this view the most important factors in connexion with the electrical disintegration process are the latent heat of liquefaction and the thermal conductivity of the disintegrating metal. A modification of Svedberg's methods for the electrical synthesis of colloids, which is said

[58] B. von Szyszkowski, *Zeitsch. physikal. Chem.*, 1913, **84**, 91 ; *A.*, ii, 685.
[59] G. Senter and A. W. Porter, *T.*, 1911, **99**, 1049.
[59a] W. J. Jones and A. Lapworth, *ibid.*, 1427.
[60] C. Benedicks, *Koll. Chem. Beihefte*, 1913, **4**, 229 ; *A.*, ii, 307.

to give much better results,[61] involves the use of a high-frequency alternating arc.

The reversibility of the coagulation of colloids in certain cases has been illustrated by experiments with one per cent. colloidal solutions of silver and sulphur.[62] The colloids were coagulated by addition of electrolytes, the latter subsequently removed by centrifugalising, and on addition of pure solvent to the original amount the colloids again passed into solution. From the results of an ultramicroscopic investigation the authors state that not only is there no change in the size of the particles after repeated coagulation and resolution, but that the individual particles retain their identity throughout.

The rate of coagulation of colloidal solutions by electrolytes has been investigated in the case of copper[63] and of aluminium hydroxide.[64] In the latter case viscosity measurements were used, the assumption being made that the same increase of viscosity always corresponds with the same alteration of the colloidal solution; in the case of colloidal copper the measurements were based on the assumption that the part of the colloidal substance which is easily separated from the solution may be regarded as the coagulated portion. The main conclusions reached in the two investigations are in entire agreement, the more important being as follows. On addition of an electrolyte there is an initial period in which little or no change occurs; when coagulation commences at the end of this period the speed at which it occurs diminishes in a continuous manner. The coagulation curves with different electrolytes are similar in type. The factor of coagulation-velocity V is connected with the concentration of electrolyte in the solution c by means of the equation $V = Lc^p$, where L and p are constants; for different electrolytes p varies between 3 and 6. The observations bear out the theory of Freundlich that electrolytes which are strongly absorbed have a great, electrolytes which are only slightly absorbed a slight, coagulating effect.

Reference may also be made to an interesting communication[64a] on the time reactions between colloidal solutions, more particularly Prussian blue and alkalis. The rate of reaction is not proportional to the hydroxyl concentration of the solutions, so that the cations are also of importance; neutral salts, contrary to what might be

[61] H. Morris-Airey and S. H. Long, *Proc. Univ. Durham Phil. Soc.*, 1913, **5**, 68; *A.*, ii, 1033.

[62] Sven Odén and E. Ohlon, *Zeitsch. physikal. Chem.*, 1913, **82**, 78; *A.*, ii, 194.

[63] H. H. Paine, *Proc. Camb. Phil. Soc.*, 1912, **16**, 430; *A.*, 1912, ii, 337.

[64] N. Ishizaka and H. Freundlich, *Zeitsch. physikal. Chem.*, 1913, **83**, 97; *A.*, ii, 486.

[64a] D. Vorländer, R. Hüberle, and W. Strube, *Ber.*, 1913, **46**, 1612; *A.*, ii, 570.

expected, accelerate the reaction in most cases. The widely prevalent view that arsenious sulphide undergoes hydrolysis when suspended in water is not confirmed.

An important series of papers[65] dealing more particularly with the importance of viscosity measurements for the elucidation of problems in colloidal chemistry cannot be referred to in detail. Reference should also be made to a very complete and interesting investigation[66] of the nature of starch jellies.

Electrolytic Dissociation.

It is a well known fact that the ionisation of many electrolytes does not follow the mass law, and many attempts have been made to find a general relationship representing the variation of ionisation with dilution. The most recent, as also one of the most important and significant,[67] will now be briefly described.

The authors propose to express the relationship between the concentration and conductivity of solutions of binary electrolytes by the general equation $(\alpha c)^2/(1-\alpha)c = K + D(\alpha c)^m$, where c is the concentration, α the conductivity ratio λ/λ_0, and K, D, and m are constants. In sufficiently dilute solutions the term involving $(\alpha c)^m$ becomes negligible in comparison with K, and the equation approaches the simple mass-action law as a limit. In concentrated solutions K becomes negligible in comparison with $D(\alpha c)^m$, and the equation assumes the well known form first put forward by Storch. It might appear at first sight that the equation is a purely arbitrary one, involving four constants, λ_0, D, K, and m (λ_0 being involved in the determination of α), but it is shown that the constants are not arbitrarily determined in all respects.

The equation has been shown to hold for the extensive data accumulated by Franklin and his co-workers for solutions in liquid ammonia, and also to solutions in liquefied sulphur dioxide. Solutions of strong electrolytes in non-aqueous solvents follow the mass-law up to $0{\cdot}001N$ concentration; at higher concentrations they follow a simplified form of the general equation. The general equation also applies to strong electrolytes in aqueous solution, for example, potassium chloride, but it cannot readily be tested for such solutions owing to the small values of the non-ionised part $(1-\alpha)c$.

Certain relationships between the ionising power of a solvent and the value of the constants K, D, and m are discussed, and it is shown that the deviations from the Nernst-Thomson rule observed

[65] W. Ostwald: W. Pauli: E. Hatschek, *Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 213; *A.*, ii, 558, 559.

[66] A. Meyer, *Koll. Chem. Beihefte*, 1913, **5**, 1; *A.*, ii, 848.

[67] C. A. Kraus and W. C. Bray, *J. Amer. Chem. Soc.*, 1913, **35**, 1315; *A.*, ii, 914.

when comparison is made at some arbitrary concentration disappear when comparison is made in terms of the constants of the general equation.

The more important results of the investigation are as follows: (1) All solutions of binary electrolytes obey the same dilution law; (2) the law of mass action is obeyed at high dilutions; (3) the divergence of the law of mass action at higher concentrations is a function of the ionic concentration αc; (4) for a given electrolyte in different solvents the trend of the conductivity curve is determined by the dielectric constant of the solvent.

The solubility of tetramethylammonium iodide in about ten organic solvents at 25° and the electroconductivity of the solutions have been measured by Walden,[68] and the remarkable result is obtained that the degree of dissociation in saturated solution is the same for all the solvents, and has the value 0·666. Preliminary experiments with saturated solutions of potassium iodide in water and in methyl and ethyl alcohols show that in this case also α is constant and equal to 0·423.

It will be appropriate to mention here that an earlier observation of Walden[69] to the effect that solutions of salts in methyl thiocyanate bring about a lowering and not a raising of the boiling point has been traced[70] to the conversion of the thiocyanate into the thiocarbimide, which has a lower boiling point than the normal ester.

A further contribution to the complicated question of the dissociation of ternary electrolytes may be mentioned.[71]

Influence of the Solvent on Velocity of Reaction.

It is well known that the nature of the solvent has a marked influence on the rate of chemical changes, and this raises such questions as whether the solvent actually takes part in the reaction and whether its effect on the speed of reaction can be connected with any of his physical properties. Although such questions cannot yet be definitely answered, considerable progress has recently been made in our knowledge of this subject. Patterson and Montgomerie[72] have measured the transformation of anis*syn*aldoxime to anis*anti*aldoxime in the presence of ethyl tartrate and a number of organic solvents, and from a comparison of their results with those

[68] P. Walden, *Bull. Acad. Sci. St. Pé'ersbourg*, 1913, 427; *A.*, ii, 566.

[69] P. Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 281; *A.*, 1906, ii, 336.

[70] A. Smits and H. Vixseboxse, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 33; *A.*, ii, 853.

[71] C. Drucker, R. Gifford, L. Gomez, and D. Kazansky, *Zeitsch. Elektrochem.* 1913, **19**, 808.

[72] T. S. Patterson and H. H. Montgomerie, *T.*, 1912, **101**, 26, 2100.

of previous observers show that solvents influence quite different reactions in a uniform matter, although the effect in one case may be retardation, in another acceleration. From this result it would appear that the property or properties of the solvents which bring this about are the same throughout.

The same problem has been attacked in a more fundamental manner on the basis of certain considerations due to van't Hoff.[73] He pointed out that the action of the solvent on the velocity is made up of its effect on the equilibrium of the reacting system and of a possible specific effect, and showed that the effect on the equilibrium could be deduced from the solubilities of the reacting substances. From the results of the first comprehensive investigation[74] carried out to test this theory—the determination of the solubility and rate of transformation of the isomeric forms of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate in a series of solvents—the conclusion was drawn that the effect of the solvents was due almost entirely to their effect in displacing the equilibrium. On the other hand, in the change of ε-chloroamylamine to piperidine hydrochloride[75] there is no relationship between the velocity of the reaction and the solubility of the substances. Further, the rate of combination of *p*-nitrobenzyl chloride and trimethylamine has been measured in over twenty organic solvents,[76] and it is shown that in this case also there is no direct connexion between rate of reaction and solubility. From these results the conclusion must be drawn that in addition to its effect in displacing the equilibrium the solvent exerts, at least in some cases, a specific (catalytic) influence on the rate of reaction.

From a general point of view it would appear unlikely that any simple relationship exists between the rate of reaction and the nature of the solvent, since it is probable that in some, but not in all, cases the solvent takes a direct part in the reaction. The former alternative is almost certainly met with in the marked influence of small amounts of water on the rate of ester formation in alcoholic solution.

Dielectric Constants of Dissolved Salts. Bearing on Electrolytic Dissociation.

It has hitherto been assumed, mainly on the authority of Nernst (1894) and of Drude (1896–97), that the dielectric constants, K, of

[73] *Vorlesungen*, 1901, **1**, 214.

[74] O. Dimroth, *Annalen*, 1910, **377**, 127 ; *A.*, 1911, ii, 31.

[75] H. Freundlich and M. B. Richards, *Zeitsch. physikal. Chem.*, 1912, **79**, 681 ; *A.*, 1912, ii, 633.

[76] H. von Halban, *ibid.*, 1913, **84**, 129 ; *A.*, ii, 937.

solvents are not greatly affected by the addition of electrolytes. This view was based mainly on experiments with aqueous solutions, but as water has itself a high dielectric constant and the solutions have a high conductivity, the effect of electrolytes on the magnitude of this property is not easy to measure. It is now shown by Walden,[77] as a result of a large number of measurements with solvents of relatively low dielectric constant (chloroform, methylene chloride, ethyl formate), and with others of relatively high dielectric constant (acetylacetone, propionitrile), that the addition of binary salts produces a very marked increase in the magnitude of the property in question. The type of the binary electrolyte has a marked effect on the magnitude of this increase, the smallest effects being due to salts of primary amines, and the largest to tetra-alkyl-ammonium salts (K for chloroform, 4·95; for a $N/10$-solution of tetraethylammonium chloride, 7·05; for a $N/5$-solution of amyl-amine hydrochloride, 5·0). From these and other results the conclusion is drawn that salts which have a high tendency to ionise (for example, tetraethylammonium chloride) possess a very large dielectric constant, whereas with weak electrolytes the reverse is the case. According to the Nernst-Thomson rule, the electrolytic dissociation of a dissolved electrolyte increases as the dielectric constant of the solvent increases. The final result, that is, the degree of electrolytic dissociation, is therefore produced by the superposition of two effects: the ionising tendency of the dissolved salt and of the solution respectively, which intensify each other, and are dependent on all the components of the solution.

As regards the nature of the solvent, the rule holds that the higher the dielectric constant of the solvent the higher the calculated dielectric constant of the dissolved salt. This is strikingly illustrated by the following table, for which tetraethylammonium iodide was used as solute, except in the case of water when potassium chloride was used:

Solvent.	K_2 (for solvent).	Dilution (mols. per litre).	K (observed).	α.	K_1 for salt (Bouty's formula).
Methylene chloride	8·3	50	9·35	small	280
Acetylacetone	26·0	100	27·2	0·70	480
Propionitrile	26·5	200	27·3	0·72	510
Acetonitrile	36·3	200	37·5	0·82	770
Water	81·7	100	90·9	0·94	12,400

The enormous increase of the dielectric constant on ionisation is illustrated by the fact that K_1 for solid potassium chloride is about 4·9, whereas in aqueous solution, according to the above table, it is about 12,000.

[77] P. Walden, *Bull. Acad. Sci. St. Pétersbourg*, 1912, 305, 1055; *J. Amer. Chem. Soc.*, 1912, **35**, 1649; *A.*, 1912, ii, 421; 1913, ii, 98.

On the basis of these results the well known deviation of strong electrolytes from the dilution law (the ionisation in concentrated solution being greater than corresponds with the law of mass action) is ascribed to a combination of three causes: (1) the increase in ionising power of the solution with increasing concentration; (2) increased ionisation of the solvent water for the same reason; (3) the effect of change in dielectric constant on ionic mobility. Whilst the first of these reasons is undoubtedly of great importance, and the third may be of influence, it does not appear to the writer that the suggested increase in the ionisation of water can be reconciled with the fact that the same value is obtained for the dissociation constant of water independently of whether it is determined in salt solutions or not. Moreover, it has recently been shown by direct experiment[78] that the ionisation of water is not increased, but, on the contrary, diminished, by the presence of salts.

Electrical Conductivity of Fused Salts.

It has been suggested that fused salts may have a certain degree of metallic conductivity in addition to electrolytic conductivity. Recent experiments[79] on the electrolysis of fused silver iodide have a direct bearing on this question. In a series of quantitative experiments at 160°, 200°, 250°, 300°, and 350° Faraday's first law was verified, so that if fused silver iodide has any metallic conductivity it must constitute only a very minute fraction of the total conductivity.

Magnetic Properties of Alloys.

The announcement in 1903 by Heusler, that many binary and ternary manganese alloys show decided magnetic properties although the component metals are not magnetic, was received with great interest, and since then a large number of investigations have been carried out with the object of throwing light on the nature of this phenomenon. The whole subject of the magnetic properties of alloys has recently been discussed before the Faraday Society,[80] and as the various contributions representing the present position of the subject are readily accessible, a brief reference to what is perhaps the most interesting question—the connexion between composition and magnetic character—will be sufficient for our present purpose.

Binary alloys of manganese with aluminium, tin, antimony,

[78] G. Poma and B. Tanzi, *Zeitsch. physikal. Chem.*, 1912, **79**, 55; *A.*, 1912, ii, 323.

[79] G. Bruni and G. Scarpa, *Atti R. Accad. Lincei*, 1913, [v], **22**, i, 438; *A.*, ii, 472.

[80] Sir R. Hadfield, E. Colver-Glauert, S. Hilpert, P. Weiss, H. K. Onnes, E. Wedekind, F. Heusler, E. Take, A. D. Ross, and T. Dieckmann, *Trans. Faraday Soc.*, 1912, **8**, 94; *A.*, ii, 17.

bismuth, boron, and arsenic are all magnetic, and this property is particularly marked in the ternary alloys of copper, manganese, and aluminium, to which the term Heusler alloys is more particularly applied. It has now been conclusively shown as regards the Heusler alloys that the maximum of magnetic properties occurs in a series of mixed crystals, the end members of which are Mn_3Al and Cu_3Al, but the further suggestion of Heusler[81] that the carriers of the ferromagnetic properties are ternary chemical compounds of the three metals has not been generally accepted.[82] The most definite connexion between composition and magnetic power has been met with in the case of the manganese-boron alloys: the maximum of magnetic properties pertains to the compound MnB, whereas MnB_2 has no magnetic character. The respective temperatures at which loss of magnetic properties occurs on heating, and this property is regained on cooling in the case of the compounds of manganese with the elements of the arsenic group, are as follows[83]: MnP, 18—25°; MnAs, 45—50°; MnSb, 310—320°; MnBi, 360—380°.

Photochemistry. New Theory of Photochemical Action.

With regard to the immense amount of work carried out in this branch of chemistry during the last year or two, reference to previous Annual Reports shows that it has been usual to describe experimental details in the sections dealing with Inorganic and Organic Chemistry respectively. The present report, therefore, is concerned mainly with results of a quite general character, and a new theory of photochemical action is discussed.

The classical photochemical reaction, the combination of hydrogen and chlorine, has now been investigated from the point of view of the influence of mass on the reaction velocity by Chapman and Underhill,[84] and by Bodenstein and Dux.[85] The first-named investigators, who used a modification of the original method of Bunsen and Roscoe, varied the concentration of the hydrogen only, and show that the rate of formation of hydrogen chloride is at first almost proportional to the partial pressure of the hydrogen from zero upwards, but the ratio of partial pressure of hydrogen to velocity of reaction rose continually in value as the proportion of hydrogen was increased. At a definite concentration of hydrogen the rate of formation of hydrogen chloride attains a maximum, and

[81] F. Heusler. *Zeitsch. anorg. Chem.*, 1909, **61**, 277; *A.*, 1909, ii, 240; *loc. cit.* (*Trans. Faraday Soc.*), p. 181.

[82] A. D. Ross, *loc. cit.*, p. 218.

[83] Hilpert, Dieckmann, and Colver-Glauert, *loc. cit.*, p. 207.

[84] D. L. Chapman and L. K. Underhill, *T.*, 1913, **103**, 496.

[85] M. Bodenstein and W. Dux, *Zeitsch. physikal. Chem.*, 1913, **85**, 297.

falls off slowly as the proportion of hydrogen is still further increased. The mixtures throughout contained a small proportion of oxygen. The suggested explanation of these results is that the light absorbed by the chlorine is all at first in the form of vibrational energy, and incapable in this form of promoting the union of hydrogen and chlorine. Part of this vibrational energy undergoes degradation to heat, and part changes to so-called actinic energy, which renders the chlorine molecules abnormally active. If the mixture contains hydrogen, part of the actinic energy is utilised in producing chemical change, the proportion being the higher the greater the concentration of the hydrogen. Bodenstein and Dux point out the limitations of the Bunsen-Roscoe method for investigations of this type, and have devised an arrangement which enables the influence of all the factors concerned in the reaction to be measured. The hydrogen and chlorine are admitted into the reaction vessel, and their pressures determined by means of a quartz glass manometer. Then the light is allowed to act for a stated time, and the amount of hydrogen uncombined is measured by freezing the chlorine and hydrogen chloride by cooling with liquid air, the pressure of the residual hydrogen being then determined. The results of Chapman and his co-workers, that with a given intensity of light the velocity of the reaction is practically independent of the hydrogen concentration above a definite value and inversely proportional to the square of the oxygen concentration, are confirmed, and it is further shown that the speed of the reaction is independent of the concentrations of hydrogen chloride and water vapour, and probably proportional to the square of the chlorine concentration.

A new theory of photochemical change is developed,[86] based on the assumption that the absorption of light energy ionises the atom into an electron and a positively charged residue, both of which can give rise to chemical changes. The reactions occurring between the positively charged residues and other molecules are termed primary reactions, and are supposed to be practically instantaneous. Their more important characteristics are as follows: The amount of action is proportional to the absorbed energy, and independent of the temperature, the concentration, and the nature of the impurities. The order of the reaction, according to the amount of absorption, is one, zero, or corresponds with Beer's law. Finally, each molecule taking part in the change uses one quantum or a very small number of quanta of energy. The secondary reactions are those brought about by the free electrons attaching themselves to neutral molecules and rendering the latter chemically active. The

[86] Bodenstein, *loc. cit.*

kinetics of these reactions are developed mathematically, treating the electron as a chemical molecule. The equations indicate that the velocity of the secondary reactions depends not only on the energy absorbed, but also on the concentrations of the reacting substances and the nature of the impurities. For one quantum of energy between 10^{-3} and 10^{6} molecules are decomposed, usually, however, more than one. The photochemical changes which have been accurately investigated are discussed from this point of view, and it is shown that ten belong to the first class and twelve to the second.

The fundamental assumption of this suggestive theory appears to be opposed to recent results,[87] which indicate that ionisation, chemical decomposition, and the formation of fog nuclei are three quite distinct action of light. Pure chlorine is not appreciably ionised by the action of ultraviolet rays, so that the atom of chlorine does not readily give up an electron under conditions which readily lead to the expulsion of electrons in the case of the electropositive elements. With reference to the reaction under discussion, it is suggested that the hydrogen atom may lose an electron, which will then combine with the chlorine atom, and result in the chemical combination of the atoms.

A year or two ago Einstein put forward a general law for photochemical decomposition on the basis of the quanta theory to the effect that the energy required for the photochemical decomposition of a gram-equivalent of a substance is Nhv, where N denotes the number of molecules in a gram-equivalent, h is the constant of Planck's radiation formula, and v is the frequency of the active vibration—in other words, one quantum of energy brings about the decomposition of a single molecule. The law has been shown by Warburg[88] to hold quite accurately for the photochemical production of ozone from oxygen, in which case 46 per cent. of the energy absorbed is regained when the ozone produced goes back again to oxygen.

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[87] E. B. Ludlam, *Phil. Mag.*, 1912, [vi], **23**, 757; *A.*, 1912, ii, 511.

[88] E. Warburg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 216; *A.*, 1912, ii, 315; compare Bodenstein, *loc. cit.*, p. 335.

INORGANIC CHEMISTRY.

During the past year a very remarkable series of papers has been published dealing with the production of neon and of helium by the passage of the electric discharge through gases at very low pressures. Whatever may be the correct interpretation of the formation of these gases, whether they are due to a synthetic process taking place, or whether they were previously occluded in the walls of the vacuum tube or in other substances submitted to bombardment by cathode rays, there is no doubt that their occurrence is one of extraordinary interest and importance.

Collie and Patterson on the one hand, and Sir J. J. Thomson on the other, have proved without any possible doubt that these gases are produced by the action of the discharge. Even if Thomson's view turns out in the end to be the correct one, the question still remains to be answered as to how these gases were occluded in the various substances in the first place. If the tentative suggestion he mentions proves to give the true solution, a new field is opened up involving the radioactivity of elements hitherto considered to be rigidly stable. Sir J. J. Thomson has also, by means of his well-known positive ray method, discovered along with the neon and helium the existence of a new gas with an atomic weight of 3, and possibly another with an atomic weight of 10. The first gas, provisionally known as X_3, seems to be produced in greater quantities than either the neon or helium.

These investigations certainly rank amongst the most important contributions to science of recent years.

Another striking paper has been published by Sir J. Dewar on the specific heats of the elements between the boiling points of nitrogen and hydrogen. He has established the fact that when the specific heats are measured at these low temperatures the atomic heats of the elements are a periodic function of their atomic weights, and that the curve representing the relation between the two has a shape very similar to Lothar Meyer's atomic volume curve.

Speaking generally of the work done in inorganic chemistry

during this last year, it is becoming more and more difficult to do justice to it within reasonable limits of space. Much of the work possesses very great intrinsic interest, as, for example, that of Stock and his co-workers on the hydrides of boron.

The report in the main follows the lines of those in previous years. It has been felt advisable to hold over an account of several branches of work, more particularly on rare earths, for a future report.

Atomic Weights.

In their report the International Committee have not recommended any change in the list of atomic weights published in 1912. They express the opinion that it is disadvantageous to make any change unless such change is thoroughly justified, since frequent alteration is liable to give rise to confusion.

During the year several papers have appeared describing new determinations of atomic weights of various elements, and of these perhaps the following deserve mention.

Helium.[1]—An accurate determination of the density of pure helium results in the fact that the weight of one litre of this gas is $0{\cdot}17856 \pm 0{\cdot}00008$. This gives the atomic weight of helium as 4·002.

Selenium.[2]—Two investigations have been carried out on the atomic weight of selenium. In the first of these the atomic weight has been arrived at through the density of hydrogen selenide. This gas was prepared by the action of water on aluminium selenide; after being dried by phosphoric oxide it was liquefied and fractionally distilled. The weight of one litre was found to be 3·6715 grams, whence the atomic weight of selenium is 79·18. In the second investigation,[3] pure selenium was oxidised to the dioxide by means of pure nitrogen peroxide carried in a stream of pure oxygen. The selenium dioxide was reduced to selenium by means of hydrazine hydrate. As a mean of several determinations carried out with great care, the atomic weight was found to be 79·141.

Tellurium.[4]—Some further work on the atomic weight of this element has been carried out, the method adopted being the synthesis of the tetrabromide. The atomic weight found was 127·479. The results of this determination still further confirm the homogeneity of tellurium, for the results obtained with various fractions of tellurium were closely similar.

[1] W. Heuse, *Ber. Deut. physikal. Ges.*, 1913, **15**, 518; *A.*, ii, 774.

[2] P. Bruylants and A. Bytebier, *Bull. Acad. roy. Belg.*, 1912, 856; *A.*, ii, 500.

[3] J. Jannek and J. Meyer, *Zeitsch. anorg. Chem.*, 1913, **83**, 51; *A.*, ii, 948; J. Meyer, *Zeitsch. Elektrochem.*, 1913, **19**, 833; *A.*, ii, 1048.

[4] W. F. Dudley and P. C. Bowers, *J. Amer. Chem. Soc.*, 1913, **35**, 875; *A.*, ii, 695.

Radium.[5]—Reference was made in last year's Report to Hönigschmid's determination of the atomic weight of radium from analyses of radium chloride. This year a further paper has appeared by Hönigschmid, giving his results of the determination of the ratio $RaBr_2/AgBr$. Six analyses with nearly one gram of radium bromide, which had been recrystallised thirty times, gave the atomic weight of radium as 225·96, a value which agrees extraordinarily well with that obtained from the analysis of the chloride. Hönigschmid criticises the work of Whytlaw-Gray and Ramsay,[6] and he corrects their values for a constant error in the reduction of the weights to vacuum. The corrected value thus obtained is $226·26 \pm 0·21$. He also has made determinations of the atomic weight by Whytlaw-Gray and Ramsay's method, namely, the conversion of radium bromide into radium chloride by heating in the current of hydrogen chloride. The mean of two experiments gave the value 225·94. Altogether Hönigschmid has made seventeen analyses of radium chloride and radium bromide, and the mean atomic weight found is $225·97 \pm 0·012$. The extreme values were 225·99 and 225·93 ($Ag = 107·88$; $Cl = 35·457$; $Br = 79·916$).

Some interesting papers have appeared on atomic weights and their relationships amongst themselves and with other properties of the elements. Two arithmetical relationships seem to exist between the atomic weight of elements and the molecular weights of compounds, both of which involve the ratio π. The first of these can be expressed as follows[7]:

$$\frac{R_1}{R_2} = \frac{\pi}{n},$$

where n is a simple integer. As an example of this relationship may be given:

$$\frac{3I}{Cl + Br + I} = \frac{\pi}{2}.$$

If Stas's atomic weights are used, the value of π is found to be 3·1417. The second relationship may be expressed by:

$$\frac{M \pm n\pi}{M' \pm n'\pi} = \frac{a}{b},$$

where n, n', a, and b are simple integers. As an example of this relationship may be given:

$$\frac{HCl + 2\pi}{NH_3 - 2\pi} = 4,$$

[5] *Monatsh.*, 1913, **34**, 283; *A.*, ii, 268.

[6] R. Whytlaw-Gray and Sir W. Ramsay, *Proc. Roy. Soc.*, 1912, A. **86**, 270; *A.*, 1912, ii, 413.

[7] P. Dampier, *J. Chim. phys.*, 1913, **11**, 260; *A.*, ii, 767.

which gives the value of π as 3·1416. It seems very probable that the relations between the atomic weights involves the ratio π, and if these relations are true, it becomes impossible to satisfy the values of the atomic weights by any single system. This has been very favourably criticised by P. A. Guye,[8] who points out that the relationships found by Dampier must certainly be taken into account in any study of atomic weight relations.

Two papers have appeared dealing with the relations between atomic weights and the physical properties of the elements. In one[9] it is shown how the heat of ionisation and the temperature-coefficient of ionic velocities are periodic functions of the atomic weights. In the second paper,[10] similar periodic relations are found between the atomic weights of the elements and their hardness, boiling points, melting points, electric conductivity, light absorption, and refractive indices.

Specific Heats.

Measurements have been published of the specific heats of helium and various diatomic gases at the ordinary temperature and at the boiling point of liquid air.[11] The specific heats at constant pressure were made by the continuous flow method.[12] The specific heat at constant volume was calculated from thermodynamical relations based on Berthelot's equation of condition. It was found generally that the ratio of the two specific heats tends to increase considerably with fall of temperature. The results obtained may be tabulated as follows:

	Temp.	Cp.	Ratio.
Helium	18°	4·993	1·660
	−188	4·934	1·673
Hydrogen	18°	6·860	1·407
	−181	5·330	1·597
Nitrogen	20°	6·983	1·400
	−181	7·162	1·468
Oxygen	20°	6 98	1·399
	−181	7·30	1·447
Air	20°	6·965	1·401
	−181	7·23	1·450
Carbon monoxide ...	18°	7·006	1·398
	−180	7·244	1·472

A very remarkable paper has been published by Dewar,[13] in

[8] *J. Chim. phys.*, 1913, **11**, 267 ; *A.*, ii, 767.
[9] N. Dhar, *Zeitsch. Elektrochem.*, 1913, **19**, 911 ; *A.*, 1914, ii, 44.
[10] W. Biltz, *ibid.*, 613 ; *A.*, ii, 855.
[11] K. Scheel and W. Heuse, *Ann. Physik*, 1913, [iv], **40**, 473 ; *A.*, ii, 183.
[12] *Ibid.*, 1912, [iv], **37**, 79 ; *A.*, 1912, ii, 19.
[13] *Proc. Roy. Soc.*, 1913, A, **89**, 158 ; *A.*, ii, 827.

which he gives the specific heats of the elements between the temperature of boiling nitrogen and boiling hydrogen. The substances were cooled in boiling nitrogen and then dropped into liquid hydrogen, a fall of temperature of 57·5°. The volume of hydrogen thus evaporated was measured. The amount of hydrogen evolved from the calorimeter when at rest was well under 10 c.c. per minute, and this was corrected for. As in each experiment the time occupied in the evolution of the hydrogen was about fifteen seconds, this correction only amounted to about 2 c.c. Certain other corrections were necessary, but they need not be described in detail. The accuracy of the work is well shown by the case of lead, the mean value of the specific heat of which was found to be 0·02399, the extreme values being 0·0247 and 0·0233. The mean value gives the atomic specific heat of lead as 4·965, whilst from Nernst and Lindemann's formula it is calculated as 5·18. At least three pieces of every substance were used. The results obtained rarely varied by more than 2 to 3 per cent., and frequently they were within 1 per cent. Altogether fifty-three elements were experimented with, about two hundred separate observations being made.

Dewar finds that when atomic specific heats are plotted against atomic weights, a periodic curve is obtained which closely resembles Lothar Meyer's atomic volume curve. It is probable that if the specific heats were taken between the boiling points of hydrogen and helium, the atomic specific heats would be very small and nearly constant. The investigation is being continued with the view of determining the molecular specific heats of a series of inorganic and organic compounds. Dewar states that until more accurate values are obtained with purer elements and with a more improved form of calorimeter, it is advisable to postpone any theoretical discussion of his results.

In connexion with Dewar's statement as to the probability of the atomic specific heats, if taken between the boiling points of hydrogen and helium, being very small and nearly constant, it is interesting to note some results of the determination of the specific heats of some metals between 0° and 100°. The specific heats[14] were determined of copper, aluminium, iron, zinc, silver, cadmium, tin, and lead, and their values at 0° are given by the formula $S = 4{\cdot}084 \times A^{-0{\cdot}95}$, when S is the specific heat, and A is the atomic weight. By extrapolation it is found that at absolute zero the atomic specific heat of the above metals has a mean value of 4·813.

[14] E. H. Griffiths and E. Griffiths, *Phil. Trans.*, 1913, A, **213**, 119 ; *A.*, ii, 753

Allotropy.

Yet another allotropic modification of sulphur has been discovered.[15] If the solution of sulphur in sulphur chloride saturated at the ordinary temperature is heated to 150° and then cooled, it dissolves a further and considerable quantity of sulphur. This cannot be explained by the formation of $S\mu$, since $S\mu$ at the ordinary temperature is only sparingly soluble in sulphur chloride, and separates out quite easily on cooling a hot solution. Systematic solubility determinations were made of sulphur in sulphur chloride which had previously been heated with varying quantities of sulphur at definite temperatures and cooled to 25°, 0°, or −60°. Again, when sulphur is heated to 125° and rapidly cooled, it becomes more soluble in sulphur chloride. These results point to a new modification of sulphur which is named $S\pi$. Further investigation shows that when sulphur is heated to 170° and rapidly cooled, it contains just as much $S\pi$ as when it is heated to 445° and rapidly cooled. Also it is found that heated sulphur is more soluble in toluene than unheated sulphur, and the solubility is greater the more solid sulphur that is present. All solutions containing $S\pi$ are deep yellow; for example, a carbon disulphide solution containing 18 atoms per cent. has a colour analogous to that of a concentrated aqueous solution of potassium chromate. On cooling such a solution to −80°, the whole of the $S\lambda$ separates out, leaving only $S\pi$ in solution. Attempts were made to obtain solid $S\pi$ by evaporation of such solutions, but at first only $S\mu$ was obtained. It was found, however, that if the solution were evaporated in a vacuum at a temperature of −80°, the residue left was almost entirely soluble in toluene, a very small quantity of $S\mu$ being left. It is extremely unlikely that solutions of $S\pi$ are really solutions of $S\mu$. Confirmatory evidence of this was found in the action of light on the solutions. Two solutions, one containing $S\lambda$ and the other containing $S\lambda$ and $S\pi$, were exposed to a strong light; in each case $S\mu$ was immediately precipitated, but much less was obtained in the case of the solution containing both $S\lambda$ and $S\pi$ than in the case of the solution containing only $S\lambda$. Clearly, if $S\lambda$ and $S\mu$ were identical, more $S\mu$ would have been precipitated in the case of the solution containing $S\lambda$ and $S\pi$.

Note may also be made of the discovery of two enantiotropic modifications of bismuth.[16] The transition temperature is 75° at 760 mm. pressure, and the transition of the α-modification into the

[15] A. H. W. Aten, *Zeitsch. physikal. Chem.*, 1912, **81**, 257; 1913, **83**, 442; *A.* ii, **40**, 580.

[16] E. Cohen and A. L. T. Moesveld, *Chem. Weekblad*, 1913, **10**, 656; *A.*, ii, 779.

β-modification is accompanied by a considerable increase in volume. The β-modification is shown to be capable of metastable existence below the transition temperature.

A. Smits[17] has made an interesting application of his theory of molecular species to the passivity of metals. He states that metals are built up of different molecular species, each of which has a different reactive power. When the metal is treated with a reagent that tends to dissolve it, the equilibrium between the molecular species will be disturbed, and if the equilibrium is only restored very slowly the metal will become passive.

Two forms of tellurium[18] have been found to exist in dynamic equilibrium with one another, the equilibrium depending on the temperature. The density varies between 6·272 and 5·949. It is pointed out that, with the exception of the atomic weight, all the constants of tellurium are to be doubted, owing to the existence of unknown amounts of Te_A and Te_B in all specimens of tellurium.

Oxidation.

Reference was made in last year's report to Rhead and Wheeler's investigation on the oxidation of carbon, in which they find that both carbon monoxide and carbon dioxide are simultaneously produced. During this year two further papers[19] have appeared, in which a theory is put forward to account for the experimental facts. It is suggested that the oxidation of carbon takes place through the intermediate existence of a complex of carbon and oxygen. When carbon is placed in an atmosphere of oxygen, the carbon atoms seize the oxygen atoms owing to there being a physico-chemical attraction between the two. On heating carbon in oxygen, the molecules become fixed, that is to say, the oxygen molecule actually enters the carbon molecule, a rearrangement taking place. With this process heat is evolved, so that some oxygen atoms acquire enough energy to seize hold of carbon atoms and depart with them in the form of carbon dioxide; some of the oxygen molecules become dissociated into atoms, and therefore leave the carbon molecules in the form of carbon monoxide.

Some doubt was thrown on the experimental work leading to this theory by H. B. Baker. He found that if absolutely dry oxygen were used, the oxidation product of carbon was almost entirely carbon monoxide, and since it is well known that carbon monoxide and oxygen when dry do not readily give carbon dioxide, these results seem to point to the fact that carbon monoxide is,

[17] *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 191; *A.*, ii, 851.
[18] E. Cohen and J. F. Kröner, *Zeitsch. physikal. Chem.*, 1913, **82**, 587; *A.*, ii, 315.
[19] *T.*, 1913, **103**, 461, 1210.

after all, the primary oxidation product of carbon. On repeating these experiments, using oxygen which had been dried for four weeks over phosphoric oxide, Rhead and Wheeler find no essential difference from their previous results, when the oxygen was dried only by concentrated sulphuric acid; that is to say, they find both carbon monoxide and carbon dioxide in the oxidation products.

In connexion with these results, it is interesting to note that both carbon monoxide and carbon dioxide have been proved to be formed when various samples of charcoal are oxidised by dilute solution of bleaching powder.[20] The amount of carbon monoxide varies, and in some cases as much as 9 per cent. was found.

The theory advanced by Rhead and Wheeler seems to be a special case comprised in the general theory of chemical reaction put forward by the writer. Every chemical molecule is surrounded by a condensed force field of electromagnetic type, and if molecules of different substances are brought together they tend to form an associated system, which in many cases has been proved to be the first stage in the chemical reaction between these two substances. The existence of these electromagnetic force fields explains the formation of the carbon oxygen complex as postulated above. A slight modification of the mechanism put forward by Rhead and Wheeler would seem to be advantageous. Similar cases of the formation of complexes are to be found in the absorption of hydrogen by palladium and of oxygen by silver respectively. In these cases the hydrogen and the oxygen have been proved to exist in the atomic condition. It is reasonable therefore to make the assumption that in the case of carbon the oxygen also exists in the atomic condition. The simultaneous production of carbon monoxide and carbon dioxide from the carbon-oxygen complex would seem to be more easily explained on these lines than on Rhead and Wheeler's explanation, according to which some of the oxygen becomes atomised during the oxidation process.

The action of ozonised oxygen on certain inorganic salts has been studied.[21] The experiments were so devised that a given volume of ozonised oxygen could be divided into two parts, one of which was used for the oxidation experiment, and the other was used for the determination of the ozone content. It was found that in the case of stannous chloride the whole molecule of ozone is effective according to the equation:

$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O.$$

In the cases of potassium arsenite, thallous and mercurous nitrates, and ferrous ammonium sulphate, only one-third of the oxygen molecule is effective, according to the usual equation: $O_3 = O_2 + O$.

[20] K. A. Hofmann, K. Schumpelt, and K. Ritter, *Ber.*, 1913, **46**, 2854; *A.*, ii, 954.

[21] Y. Yamauchi, *Amer. Chem. J.*, 1913, **49**, 55; *A.*, ii, 131.

In the case of the thallous salts the thallic oxide precipitated can be collected and weighed, and the method affords an accurate quantitative method for the estimation of ozone.

An interesting investigation[22] may be mentioned here, namely, the action of nitric acid on certain metals and alloys. In the cases of copper and silver in the presence of dilute nitric acid, approximately half the nitric acid is reduced to nitrous acid. The experimental results show that with silver the following expresses the reaction:

$$2Ag + 2HNO_3 = AgNO_3 + AgNO_2 + H_2O.$$

In the case of copper the reactions are most probably as follows:

$$3Cu + 6HNO_3 = 3Cu(NO_3)(NO_2) + 3H_2O,$$

$$3Cu(NO_3)(NO_2) + 2HNO_3 = 3Cu(NO_3)_2 + H_2O + 2NO.$$

No gas is given off when dilute nitric acid is used, and the amount of reaction taking place is increased by the addition of free nitrous acid.

Valency.

Further work has been carried out by F. Ephraim[23] on the ammine derivatives of bivalent metals since that described in last year's report. Certain errors have been found to be liable in the dissociation pressure measurements of the ammines due to incomplete drying, and to the absorption of air by the finely divided compounds. Every precaution was taken to avoid these errors, and the results as to the constancy of the tension-moduli have been confirmed. Calculation from the Nernst equation shows that in the case of the hexammines of bivalent metals dissociation occurs by the splitting off of one molecule of ammonia. This, however, is not the case with the hydrate compounds, this perhaps being due to the formation of solutions in the case of these compounds. Investigation has been extended to the study of the ammines of the sulphates of nickel, cobalt, iron, copper, manganese, zinc, cadmium, mercury, tin, lead, calcium, strontium, and barium. The results obtained were exactly analogous to those previously recorded for the halogen salts. It was again found that the value of

$$\sqrt[3]{T}.\ \sqrt[3]{v}$$

is constant, where T is the absolute temperature at which the ammonia pressure is equal to 500 mm., and v is the atomic volume. The mean value for the hexammines and pentammines was 13·8. It was also found that the value of:

$$\sqrt{T}.\ \sqrt[3]{v}$$

[22] J. H. Stansbie, *J. Soc. Chem. Ind.*, 1913, **32**, 311; *A.*, ii, 501.

[23] *Zeitsch. physikal. Chem.*, 1913, **81**, 513, 539; **83**, 196; *A.*, ii, 129, 130, 496; *Ber.*, 1913, **46**, 3103, 3742; *A.*, ii, 1061; 1914, i, 17.

was constant, being about 36·5. The ammines of cadmium sulphate were exceptional, with values 16·1 and 42·3 respectively. The modulus T_I/T_{SO_4} in the cases of nickel, cobalt, iron, manganese was 1·22, and that of cadmium and zinc 1·05 to 1·13. The hexammine derivatives of various nickel salts were compared, and it was found generally that the stronger the acid the more stable is the ammine; certain exceptions were, however, noted. The stability of these ammines is approximately analogous to that of the corresponding ammonium salts. It was found that very similar results were obtained with the derivatives of the halogen salts of nickel, cobalt, iron, manganese, copper, cadmium, and zinc, in which methylamine, ethylamine, propylamine, dimethylamine, and trimethylamine were used in place of ammonia; substituted hexammines were only obtained in the case of cobalt, nickel, and manganese, and an increasing difficulty in the preparation of these hexammines was found with increase of molecular weight of the substituted amines. In spite of these difficulties, the conclusions drawn from the ammonia compounds were again confirmed, and certain new observations made. For example, it was found that the values of $\sqrt[3]{T}$. $\sqrt[3]{v}$ were constant, and also the moduli:

$$\frac{T_I}{T_{Br}}, \frac{T_{Br}}{T_{Cl}}, \frac{T_I}{T_{Cl}},$$

were constant for the same amine.

Since nickel iodide shows the greatest affinity and tendency to form double compounds with ammonia and substituted ammonias, these ammines were compared and arranged in order of their stability. It was found that this series runs parallel with the molecular volumes of the bases, and with the values of $\frac{273+T}{P}$ where T and P are the critical temperatures and pressures of the bases. These investigations have been criticised adversely,[24] but Ephraim has shown that these criticisms are unfounded.[25]

Electric Discharge.

A most remarkable series of papers has appeared during the year on the production of neon and helium in vacuum tubes under the influence of the electric discharge. Some time ago it had been noticed by Collie that many minerals change colour when bombarded by cathode rays, and that this change of colour is especially noticeable in the cases of sodalite and fluorspar. When the gases

[24] W. Biltz, *Zeitsch. physikal. Chem.*, 1913, **82**, 688; *A.*, ii, 404; F. Friedrichs, *ibid.*, 1913, **83**, 242; *A.*, ii, 497.

[25] *Zeitsch. physikal. Chem.*, 1913, **83**, 257; **84**, 98; *A.*, ii, 578, 677.

in the vacuum tubes in which the bombardment had been carried out were pumped out and analysed, they were found to contain small quantities of neon. Ramsay had also found that on pumping out and analysing the residual gases in old *X*-ray bulbs they contained helium and a small quantity of neon.[26].

During this year this phenomenon has been independently investigated by Collie and by Patterson, and the results were published jointly.[27] Some calcium fluoride was prepared in the purest possible condition, and this was submitted to bombardment by cathode rays. The gases evolved consisted mainly of oxygen, hydrogen, and carbon monoxide. They were sparked, and then treated with charcoal cooled by means of liquid air. A small amount of neon was then found. A sample of glass wool was taken, and, after being cleaned with potassium dichromate and concentrated sulphuric acid, it was washed and dried at 120°. It was then exposed to the bombardment, and an analysis of the gases produced showed the presence of neon. The glass wool was then taken out of the tube, and about 3 to 4 c.c. of hydrogen was let into the tube, little by little, the pressure being kept low. The tube was heated during the passage of the discharge, and after some time the hydrogen was pumped out and found to contain a small quantity of neon. It is obvious that the neon was either formed inside the tube or that it leaked in. A series of blank experiments proved conclusively that no such leak had occurred. A large amount of the glass used in the vacuum tubes was powdered, washed with chromic acid, and heated in an exhausted tube until it fused. The gases evolved contained no neon. Similarly, the electrodes, which were made of aluminium, were heated in a vacuum until they fused; a considerable quantity of hydrogen was obtained, but no neon. The possibility still remained that the glass walls of the vacuum tubes might be porous to neon under the influence of cathode rays. The discharge tube therefore was then sealed inside another tube, which was connected to a second mercury pump. The wires carrying the current to the electrodes of the inner tube were so insulated that no discharge took place in the outer tube. The outer tube was filled with neon up to about half an atmosphere pressure, while hydrogen was admitted to the inner tube as in the previous experiment. After the discharge had passed through the inner tube for some time, the hydrogen was pumped out, and was found to contain the same amount of neon as usual. The neon in the outer tube was then replaced by helium, and after the experiment was finished no

[26] Sir W. Ramsay and J. N. Collie, *Nature*, 1912, **89**, 502.
[27] *T.*, 1913, **103**, 264.

helium was found in the inner tube, but only the usual amount of neon. When the experiment was carried out with the outer tube completely exhausted, the usual amount of neon was found in the residues pumped from the inner tube. A little oxygen was then let into the outer tube and pumped out again. On treatment of this oxygen with charcoal cooled by means of liquid air, an uncondensable residue was obtained about fifty times the volume obtained from the inner discharge tube, and this residue consisted mainly of helium with a small quantity of neon. When oxygen was admitted into the outer tube to a pressure of about 15 mm. with hydrogen as usual in the inner tube, the same amount of neon was found in the residues in the inner tube, while the residue from the outer tube gave nearly pure neon with a little helium. According therefore to whether the outer tube was entirely exhausted or contained a small quantity of oxygen, helium containing a little neon or neon containing a little helium was found in the outer tube. These experiments were independently carried out by both Collie and Patterson. Sir J. J. Thomson[28] has given an account of a long series of experiments which he has carried out on somewhat similar lines. His method of investigation was to submit the gases from a vacuum tube, through which various types of discharge had been made to pass, to analysis by his well-known positive ray method. He in this way discovered the existence of a new gas, having an atomic weight of 3, as well as one with an atomic weight of 20, which is probably neon. He points out that there is no obvious connexion between the nature of the gas experimented with and the appearance of these lines. The line of the gas having the atomic weight 3 was seen when the vacuum tube was filled with hydrogen, nitrogen, air, helium, or mixtures of hydrogen and oxygen. The experiments were undertaken with the object of finding the circumstances which favour the production of the gas X_3, and to test whether this gas was triatomic hydrogen or a new element. He found that the conditions favourable to the production of X_3 generally give helium and neon. In the majority of cases when traces of helium and neon were found, X_3 was present in large quantities. Two vessels were used, one in which the gases were treated with the positive rays, and another in which the various processes were tried for generating X_3. The two vessels were connected through a stop-cock. When the generating processes were finished, some of the gas could thus be admitted into the testing vessel and examined. The most plentiful supply of X_3 was obtained by: (1) bombarding metals and other substances with cathode rays; (2) discharge from

[28] *Nature*, 1913, **90**, 645.

a Wehnelt cathode through gases at low pressure; (3) arc discharge in gases at comparatively high pressures. The following results were obtained with the arc discharge in hydrogen at 3 cm. pressure, using iron electrodes. After the arc had been passed for about an hour, X_3, helium, and neon were found. The experiments were repeated next day, and gave the same results; on the third day, the same electrodes still being used, the arc was passed through oxygen. The X_3 line was much fainter, and the presence of helium and neon very doubtful. The experiment was again repeated on the fourth day, and this time none of the lines were seen. This seems as if the production of these gases was due to hydrogen, but the replacement of the oxygen by hydrogen, still using the same electrodes, gave no result. On using new electrodes, the three substances were again obtained. This clearly points to the fact that the electrodes were the source of these gases. Exactly similar results were obtained when certain substances were bombarded by cathode rays. When a substance was bombarded by cathode rays, considerable quantities of X_3, helium, and neon were obtained at first; the amount steadily decreased until no more was produced. An old sample of lead was found to give off considerable quantities of these gases. Chemically pure lead was found to give off much less, while freshly precipitated lead gave none. The addition of hydrogen and oxygen does not seem to increase the amount of gases produced, and the experiments seem to prove conclusively that the gases are always obtained from the substances bombarded. It is surprisingly difficult to get rid of these gases from a given substance by ordinary methods. For example, a sample of lead was kept boiling in a vacuum for about three to four hours; no trace of helium or X_3 was evolved; the lead, however, on being bombarded by cathode rays, was found to give off both helium and X_3.

Collie and Patterson,[29] on the other hand, find that electrodes are not necessary for the production of neon, for if a powerful oscillating discharge is passed through a coil of wire wound round a bulb containng a little hydrogen, helium and neon are to be found in the hydrogen. They pointed out that all mercury vapour must be removed from the hydrogen. When a heavy discharge is passed through a vacuum tube, very considerable quantities of hydrogen can be made to disappear. A gas is produced which gives a carbon spectrum. This gas disappears when sparked with mercury vapour, and it is not easily condensed by liquid air, nor is it oxidised by sparking with oxygen. Possibly this gas is the same as X_3, described by Sir J. J. Thomson. Collie and Patterson's

[29] *P.*, 1913, **29**, 217.

results have been independently confirmed by J. I. O. Masson.[30] He finds that after some time neon ceases to be formed in the discharge tube, but if a mixture of oxygen and hydrogen be added, neon again begins to form. The question arises at once as regards the origin of the helium and neon in these experiments. Whereas Collie and Patterson and also Ramsay incline to the view that they are the production of a synthetic process, Sir J. J. Thomson holds the view that they are actually contained in the glass or the metals, and that they are evolved under the influence of the discharge. The difficulty in connexion with the latter view is the question as to how the gases find their way into these substances in the first place. For example, Thomson points out that X_3 does not occur to any appreciable extent in the atmosphere. He says that he has sometimes ventured into the speculation whether they do not represent the partly abortive attempts of ordinary metals to imitate the behaviour of radioactive substances; whereas in these substances the α-particles and the like are emitted with such velocity that they get clear away from the atom, in ordinary metals they have not sufficient energy to get clear, but cling to the outer parts of the atom, and have to be helped by the cathode rays to escape. If this view of Sir J. J. Thomson's is correct, the question arises as to the other products of radioactive degradation of the metals. Possibly, of course, these products may be non-volatile, and consequently may not be capable of detection by the methods of experiments used by these investigators.

Some years ago the writer put forward the view that the various well-known phenomena observed in the electric spark between metallic electrodes such as the enhanced lines may be due to an assisted radioactive degradation of the metals. If the X_3 and helium can be α-particles arising from these radioactive changes, then the enhanced lines may be due to other products of the change. It would be very interesting to know whether any experimental methods would reveal the presence of the enhanced line spectrum of lead, for example, or platinum, in these discharge tubes.

Colloids.

Reference was made in last year's report to the preparation of certain of the organosols.[31] Similar organosols of palladium and platinum have now been prepared.[32] The method of preparation is briefly as follows: lanolin is impregnated with an aqueous solution

[30] *P.*, 1913, **29**, 233.
[31] *Ann. Report*, 1912, 54.
[32] C. Amberger, *Kolloid. Zeitsch.*, 1913, **13**, 310, 313; *A.*, 1914, ii, 60.

of either platinous or palladous chloride; it is then triturated with alkali carbonate, and finally treated with a solution of hydrazine hydrate. The lanolin acts as a protective colloid, and the organosols so obtained are soluble in chloroform, carbon tetrachloride, ether, light petroleum, etc. The preparation made in this way contained as much as 16 per cent. of palladium and 18 per cent. of platinum. In an exactly similar way an organosol of platinous hydroxide was prepared containing as much as 31·1 per cent. of $Pt(OH)_2$.

It has been found that if the fusions obtained by the action of magnesium, potassium, or sodium on boron trioxide are extracted first with hydrochloric acid and then several times with water, an aqueous filtrate is obtained, which possesses a decided colour, and contains a colloidal boron in solution.[33] These solutions are very readily oxidised and very readily coagulated; they contain about 0·06 per cent. of boron. The colour of the solution varies according to the metal used in the reduction of the boron trioxide. If magnesium or potassium is used, the solution has a reddish-brown colour, but when sodium is used the solution is blue.

A simple method has been published of obtaining colloidal silver solutions.[34] When dry pyridine solutions of silver nitrate and pyrogallol are mixed, a pale yellow solution is obtained, which on treatment with water gives solutions of colloidal silver. The colour of these solutions varies from yellow to orange, and finally violet, by transmitted light. When the solution contains 0·05 per cent. of silver it is fairly stable, and the colloid may be separated by centrifugalisation. Analogous results were also obtained with cupric sulphate.

The preparation has also been described of colloidal solutions of silver and mercuric sulphides by mixing dry pyridine solutions of hydrogen sulphide and silver nitrate or mercuric acetate.

Group I.

Some experiments on Schützenberger's allotropic copper[35] have led to the conclusion that it is colloidal, and its production has been explained by the protective colloid theory.[36] Cupric acetate is partly hydrolysed in solution with the formation of a basic salt or the hydroxide which remains in suspension. This wanders to the cathode during the electrolysis, and acts as a protective colloid

[33] A. Gutbier, *Kolloid. Zeitsch.*, 1913, **13**, 137; *A.*, ii, 860.
[34] A. Pieroni, *Gazzetta*, 1913, **43**, i, 197; *A.*, ii, 393.
[35] *Compt. rend.* 1878, **86**, 600; *A.*, 1878, 548.
[36] T. R. Briggs, *J. Physical Chem.*, 1913, **17**, 281; *A.*, ii, 506.

to the copper there deposited. The metal, therefore, is precipitated in the form of a solid gel.

The alkali metals have been prepared in an absolutely pure state by heating the anhydrous chlorides with metallic calcium.[37] An exhaustive study has been made of the properties of these metals, of which the following may be quoted:

	Na.	K.	Rb.	Cs.
Density at 0°	0·9723	0·859	1·525	1·903
Critical temperature	2025°	1965°	1857°	1627°

The increase of electropositivity with rise in atomic weight is well shown by the following figures, which represent the lowest temperatures at which any action with water can be detected:

Na, −98°; K, −105°; Rb, −108°; Cs, −116°.

The electrical properties of these elements are dealt with in a second paper.[38]

The preparation of ammonium hydroperoxide has already been described.[39] It has now been found possible by the same method to prepare ammonium peroxide.[40] Dry ammonia is led into an absolute ethereal solution of hydrogen peroxide (98 per cent.) at −10°; in a short time crystals are obtained of the ammonium hydroperoxide, $NH_4O_2H[(NH_4)_2O_2+H_2O_2]$. These crystals melt at 14°. If the action of ammonia is continued, a heavy, oily layer separates, and this oil can be frozen at −40°. The crystals thus obtained can be washed with ether at −40°, and are found to be ammonium peroxide, $(NH_4)_2O_2$. The compound begins to lose ammonia at −10°, and melts at −2°; it readily loses ammonia, and after remaining all night at +2° it gives pure crystals of the hydroperoxide.

The preparation of pure anhydrous sodium and potassium hydrosulphides by the action of hydrogen sulphide on the ethoxides of these metals dissolved in absolute alcohol, and subsequent precipitation by the addition of benzene or ether, was described two years ago.[41] The work has been followed up by a study of the preparation of pure anhydrous sodium monosulphide.[42] The reaction between sodium ethoxide and sodium hydrosulphide is found to be reversible, and. although sodium monosulphide can be prepared by the mutual action of these substances in alcoholic solution, using an excess of sodium ethoxide, yet this method is not satisfactory,

[37] L. Hackspill, *Ann. Chim. Phys.*, 1913, [viii], **28**, 613; *A.*, ii, 503.

[38] L. Hackspill and W. Broniewski, *ibid.*, 1913, [viii], **29**, 455.

[39] P. G. Melikov and L. Pissarjevski, *Ber.*, 1897, **30**, 3144; 1898, **31**, 152, 446; *A.*, 1898, ii, 161, 219, 292.

[40] J. D'Ans and O. Wedig, *ibid.*, 1913, **46**, 3075; *A.*, ii, 1051.

[41] A. Rule, *T.*, 1911, **99**, 558.

[42] J. S. Thomas and A. Rule, *ibid.*, 1913, **103**, 871.

owing to the difficulty of removing the sodium ethoxide from the salt. By heating sodium hydrosulphide with gradual rise of temperature and continuous removal of the hydrogen sulphide it has been found possible to obtain a quantitative yield of sodium sulphide, Na_2S. This method was found necessary owing to the fact of the dissociation of the hydrogen sulphide with the resulting formation of varying amounts of polysulphides. The Na_2S obtained is therefore coloured strongly yellow. When prepared by the method described the Na_2S is a faintly buff powder, and only contains very small traces of polysulphide sulphur.

Group II.

Metallic glucinum has been obtained by the electrolysis of a fusion consisting of sodium fluoride (one mol.) and glucinum fluoride (two mols.).[43] A nickel crucible is used as cathode and a carbon rod as anode. The current used was from 7 to 10 amperes at 15 volts. The crystals of glucinum thus obtained had a density of 1·842. They cannot be melted in air to form a compact mass owing to surface oxidation. If, however, the crystals are compressed and heated in an electric vacuum furnace a compact mass is obtained. The metal melts at $1280° \pm 20°$, and is not very easily attacked by alkalis.

Metallic barium[44] may very readily be obtained in a pure state by heating a mixture of silicon and barium oxide in an exhausted steel tube, when the following reaction takes place:

$$3BaO + Si = BaSiO_3 + 2Ba.$$

The barium distils away, and is deposited in the cooler portions of the tube.

A series of phosphates of glucinum has been described.[45] By the reaction between glucinum hydroxide and phosphoric acid, monoglucinum orthophosphate, $GlH_4(PO_4)_2$, was obtained as colourless, very hygroscopic leaflets; triglucinum orthophosphate, $Gl_3P_2O_8,6H_2O$, was obtained as a loose precipitate by the action of disodium phosphate on glucinum salts in the presence of acetic acid. In the presence of sodium hydroxide, a basic orthophosphate is precipitated having a constitution $2Gl_3P_2O_8,GlO,13H_2O$. By precipitation of glucinum salts with sodium pyrophosphate, glucinum pyrophosphate, $Gl_2P_2O_7,9H_2O$, was obtained as a white, amorphous precipitate. The following metaphosphates were also prepared: $Gl(PO_3)_2$ and $2Gl(PO_3)_2GlO$. Glucinum phosphite,

$$4GlHPO_3,GlO,7H_2O,$$

and glucinum hypophosphite, $GlH_4P_2O_4$, have also been obtained.

[43] F. Fichter and K. Jablczynski, *Ber.*, 1913, **46**, 1604; *A.*, ii, 594.

[44] C. Matignon, *Compt. rend.*, 1913, **156**, 1378; *A.*, ii, 504.

[45] B. Bleyer and B. Müller, *Zeitsch. anorg. Chem.*, 1912, **79**, 263; *A.*, ii, 137.

Group III.

Some further work has been carried out on the hydrides of boron.[46] In last year's report two hydrides of boron were described, namely, B_4H_{10} and B_6H_{12}. When the former compound is kept at the ordinary temperature it slowly undergoes decomposition, and the only gaseous products are hydrogen and a third boron hydride having the formula B_2H_6. This reaction is catalysed by ultra-violet light, and at 100° the decomposition is completed in a few hours. The compound B_2H_6 is a colourless gas, which boils at −87° to −88°; it is more stable than B_4H_{10}, and reacts with water according to the following equation:

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2.$$

This afforded a method of analysis of the compound, and it was also analysed by explosion with excess of air. The density of the compound was found to be 27·8, the theoretical value for B_2H_6 being 28. It may be pointed out that the formula B_2H_6 shows the existence of boron in a quadrivalent condition. The compound is stable when pure and stored over mercury at the ordinary temperature, but in the presence of air it tends to give compounds containing oxygen. On heating, B_2H_6 decomposes to give hydrogen and a series of solid hydrides of boron.[47] If a horizontal tube filled with B_2H_6 is heated along one-half of its length to a temperature of 115° to 120° during forty-eight hours, the other half of the tube being kept cooled, long needles are deposited, which on analysis are found to have the constitution $B_{10}H_{14}$. Altogether, three solid boron hydrides are formed by the decomposition of B_2H_6, one of which is volatile in a vacuum, namely, $B_{10}H_{14}$; the other two are not volatile, and one of these is colourless and soluble in carbon disulphide, and the other is yellow and insoluble in carbon disulphide. The compound $B_{10}H_{14}$ is soluble in alcohol, ether, or benzene, and is not acted on by water. It melts at 99·5°; at 600° to 700° it decomposes into boron and hydrogen. Its molecular weight was determined by the freezing point of its solutions in benzene. The two other hydrides of boron have not yet been completely investigated, but it would seem that the yellow compound contains five atoms of boron to four atoms of hydrogen, whilst the colourless compound has twelve atoms of boron in the molecule. Certain other compounds of boron and hydrogen still remain to be investigated.

Some doubt has been thrown on the existence of aluminates as definite compounds,[48] the suggestion being made that the solubility

[46] A. Stock and K. Friederici, *Ber.*, 1913, **46**, 1959; *A.*, ii, 699.

[47] A. Stock, K. Friederici and O. Priess, *ibid.*, 3353; *A.*, ii, 1053.

[48] E. G. Mahin, D. C. Ingraham and O. J. Stewart, *J. Amer. Chem. Soc.*, 1913, **35**, 30; *A.*, ii, 139.

of aluminium hydroxide in alkali is largely due to its colloidal properties. In a more recent paper this conclusion has been disproved.[49]

A series of electromotive force measurements with solutions of aluminium chloride during the precipitation and redissolving of the aluminium hydroxide on the addition of alkali has proved that a reaction takes place between exactly one molecule of $Al(OH)_3$ and one molecule of NaOH or KOH; in other words, aluminates must exist with the formula $KAlO_2$ or $NaAlO_2$.

Group IV.

The heats of combustion of diamond and graphite have been determined and found to be 7896 ± 3 and 7854 ± 1 calories per gram respectively.[50] The latter seems generally to be independent of the salts of the graphite. Purified graphite from cast iron from the blast furnace gave a value of 7855 to 7865 calories, which is very near the value given above.

Some work has been carried out on the production and properties of red lead.[51] Red lead is shown to exist in two forms, one crystalline and the other amorphous, and its specific gravity varies from 8·32 to 9·16. The optimum temperature for production of red lead varies with the starting material used. About 425° to 430° is best for white lead, 450° to 470° for litharge and lead sponge, and about 450° for converting lead hydroxide and metallic lead into red lead. It would seem that 450° is most probably the temperature at which red lead can be most economically produced from any suitable starting material. At 525° to 530° red lead is rapidly reduced to litharge. Both yellow and red litharge are more slowly roasted to red lead when they have been treated with water.

The conversion of litharge into red lead in an atmosphere of oxygen has been studied at temperatures between 325° and 520°, and under pressures varying from 1 to 12 atmospheres.[52] It was found that the equilibrium is independent of the pressure, although it is sooner arrived at with increasing pressure. At a temperature of from 470° to 480° a quantitative yield of red lead was obtained in three hours; above and below this temperature the yield is smaller.

In view of the theory of the production of petroleum deposits,

[49] W. Blum, *J. Amer. Chem. Soc.*, 1913, **35**, 1499 ; *A.*, ii, 963.
[50] W. A. Roth and H. Wallasch, *Ber.*, 1913, **46**, 896 ; *A.*, ii, 384.
[51] O. W. Brown and A. R. Nees, *J. Ind. Eng. Chem.*, 1912, **4**, 867 ; *A.*, ii, 410.
[52] J. Milbauer, *Chem. Zeit.*, 1912, **36**, 1436, 1484 ; *A.*, ii, 138.

some interesting analyses have been published of the gases evolved by the action of water on the carbides of uranium, thorium,[53] and the metals of the cerium group.[54] The carbides of uranium and thorium give mixtures of hydrogen, methane, ethane, propane, butane, ethylene, propylene, and homologues, together with some acetylenic hydrocarbons. In the case of the cerium metal carbides, no methane is produced, but there are found acetylene, allylene, and the higher homologues, together with small quantities of ethylene, ethane, and homologues; some free hydrogen is present, and therefore it is possible that the ethylene and ethane hydrocarbons are formed by the hydrogenation of acetylene and its homologues. The metal is always converted into the hydrated sesquioxide.

Group V.

Some doubt has been thrown on the method of formation of Strutt's active nitrogen.[55] The view has been put forward that its formation is due to the presence of small quantities of oxygen. On the other hand, Strutt[56] more recently has published results which prove that the presence of oxygen is not necessary, since 2 per cent. of oxygen entirely stops its formation. This has also been independently confirmed.[57]

Some chemical reactions of active nitrogen have been studied.[58] If the active nitrogen is passed into the vapours of mercury, cadmium, zinc, arsenic, sodium, and sulphur, the nitrides of these elements are formed, and they give ammonia when treated with water or with alkali. Sulphur chloride, when treated with active nitrogen, gives the ordinary yellow nitrogen sulphide. Acetylene, benzene, pentane, methyl bromide, ethyl iodide, ethyl chloride, and ether, when treated with active nitrogen, all give hydrogen cyanide.

Some further study[59] has been made of the alkali metal phosphides, M_2P_5, mentioned in last year's report.[60] These compounds when treated with very dilute acetic acid give a yellow solid, which is found to be H_2P_5. The solid hydrogen phosphide[61] previously

[53] P. Lebeau and A. Damiens, *Compt. rend.*, 1913, **156**, 1987; *A.*, ii, 700.

[54] A. Damiens, *ibid.*, 1913, **157**, 214; *A.*, ii, 777.

[55] F. Comte, *Physikal. Zeitsch.*, 1913, **14**, 74; *A.*, ii, 210; E. Tiede, *Ber.*, 1913, **46**, 340; *A.*, ii, 210.

[56] *Physikal. Zeitsch.*, 1913, **14**, 215; *A.*, ii, 316.

[57] A. Koenig and E. Elöd, *ibid.*, 165; *A.*, ii, 316.

[58] R. J. Strutt, *Proc. Roy. Soc.*, 1913, A, **88**, 539; *A.*, ii, 696.

[59] L. Hackspill, *Compt. rend.*, 1913, **156**, 1466; *A.*, ii, 584.

[60] *Ann. Report*, 1912, 60.

[61] A. Stock, W. Böttcher and W. Lenger, *Ber.*, 1909, **42**, 2839; *A.*, 1909, ii, **727**.

described, on being heated in a vacuum to 80°, gives gaseous hydrogen phosphide, and leaves a residue of H_2P_5. This substance had acid properties, and the phosphides, K_2P_5, Rb_2P_5, etc., may be prepared from it.

Two years ago it was shown that hydrazine sulphate is decomposed by liquid ammonia[62] according to the following equation:

$$N_2H_4,H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 + N_2H_4.$$

Since ammonium sulphate is insoluble in liquid ammonia, it is pointed out that this might give a practical method for the preparation of hydrazine. The reaction has now been further studied,[63] and it is proved to be quantitative, a 90 to 95 per cent. yield of hydrazine being obtained. The process is carried out in an apparatus especially designed for the extraction of substances by liquefied gases. In the experiments described, the apparatus is made of glass, but it might easily be constructed of iron, and then would be suitable for the preparation of hydrazine on a commercial scale.

Hydrazine nitrite may be prepared by mixing solutions of barium nitrite and neutral hydrazine sulphate.[64] The filtrate from the barium sulphate is evaporated in a vacuum over phosphoric oxide. The white residue may be crystallised from a mixture of alcohol and ether. It forms hygroscopic crystals, and explodes violently on being struck and less violently on heating. It decomposes according to the equation: $N_2H_4HNO_2 = NH_3 + N_2O + H_2O$. As this reaction is accelerated by free nitrous acid, it is obvious that hydrazine dinitrite cannot be obtained.

Some interesting work has been carried out on some of the oxides of nitrogen. In the case of the tetroxide,[65] the vapour-pressures were determined between the temperatures of $-40{\cdot}5°$ and $-11°$. The calculations of the vapour-pressures were made from Schreber's formula,[66] and, as these calculated values were smaller than those actually obtained, it is clear that some of the N_2O_4 in the gaseous phase is dissociated into NO_2 even at these low temperatures. The amount of the dissociation increases from 0·06 at $-40{\cdot}5°$ to 0·084 at $-10{\cdot}8°$.

It would seem that in the case of nitrogen pentoxide[67] none of the data concerning its physical constants hitherto published is correct, since it appears never to have been prepared in a pure

[62] A. W. Browne and T. W. B. Welsh, *J. Amer. Chem. Soc.*, 1911, **33**, 1728; *A.*, 1911, ii, 1084.

[63] F. Friedrichs, *ibid.*, 1913, **35**, 244; *A.*, ii, 316.

[64] F. Sommer, *Zeitsch. anorg. Chem.*, 1913, **83**, 119; *A.*, ii, 952.

[65] F. Russ, *Zeitsch. physikal. Chem.*, 1913, **82**, 217; *A.*, ii, 186.

[66] *Zeitsch. physikal. Chem.*, 1897, **24**, 651; *A.*, 1898, ii, 153.

[67] F. Russ and E. Pokorny, *Monatsh.*, 1913, **34**, 1027, 1051.

state. An account has been given of its preparation by the well-known method of the fractional distillation of a mixture of concentrated nitric acid and phosphoric oxide. The vapours of nitrogen pentoxide thus obtained are, however, far from pure. The distillation is carried out in a stream of ozonised oxygen, and the mixed gases passed through a tube containing more phosphoric oxide. In this way complete dehydration of the nitrogen pentoxide is obtained, and all tendency for it to dissociate into lower oxides of nitrogen is prevented by the ozone. The nitrogen pentoxide is thus obtained in an absolutely pure state, and may be completely condensed at $-80°$. The vapour-pressures of this substance have been determined between the temperatures of $-80°$ and $+17{\cdot}5°$. It is found that above 0° the vapour is partly dissociated. Inasmuch as the pressure reaches one atmosphere before the substance melts, it may be pointed out that nitrogen pentoxide has no true melting point or boiling point.

A further investigation has been made on the so-called nitrogen hexoxide, NO_3, which is produced when nitric oxide is passed into liquid oxygen.[68] This substance, when suspended in liquid oxygen, is coloured green, and as the oxygen boils away the fine flocks unite to a compact powder, which has a dull greyish-blue colour. It appears that this change of colour is accompanied by a chemical decomposition, and that a loss of oxygen occurs. The dull blue compound has been obtained free from oxygen by repeated washing with liquid nitrogen. It is found that during the washing a certain amount of oxygen is given off, and that the resulting dull blue powder has a formula NO_2 or N_2O_4. It is obvious that the substance is not the same as the ordinary nitrogen tetroxide, because the latter substance exists as white crystals at low temperatures. It is concluded from these experiments that the green substance which is produced when nitric oxide is passed into liquid oxygen is the nitrogen hexoxide, NO_3, and that on washing with liquid nitrogen it loses a portion of its oxygen, and is converted into an isomeride of nitrogen tetroxide. This substance is named nitrogen *iso*tetroxide.

An exhaustive study has been made of the physical constants of nitrosyl chloride.[69] The nitrosyl chloride was prepared by three different methods; a mixture of chamber crystals and potassium chloride, previously dried in a vacuum over phosphoric oxide, was heated to about 80°. In the second method pure chlorine and nitric oxide, after drying by means of sulphuric acid, were allowed to mix and to pass over animal charcoal at about 50°. It was

[68] F. Raschig, *Zeitsch. anorg. Chem.*, 1913, **84**, 115; *A.*, 1914, ii, 48.

[69] E. Briner and Mlle. Z. Pylkov, *J. Chim. phys.*, 1912, **10**, 640; *A.*, ii, 317.

found, however, that the animal charcoal was not necessary for the union between the two gases, as just as good a yield of nitrosyl chloride was obtained by simply mixing the gases at the ordinary temperature. The third method of preparation was based on the reaction between hydrogen chloride and nitrogen trioxide. The stream of hydrogen chloride was led into the nitrogen trioxide in a vessel cooled by a freezing mixture. The following reaction takes place: $N_2O_3 + 2HCl = 2NOCl + H_2O$; when the reaction was carried out in the presence of phosphoric oxide, nitrosyl chloride was obtained free from water. In each case it was found necessary to purify the substance, and this was done by a series of fractional distillations and recrystallisations. It was found that the density of the compound varies from 1·550 at $-55°$ to 1·221 at $+49°$. The values of the surface tension, according to Ramsay and Shields' method,[70] show evidence of a slight amount of association, but from the formulæ of Kistiakowski,[71] or Dutoit and Mojoïu,[72] or Walden,[73] it appears that nitrosyl chloride is unimolecular in the liquid state. The vapour pressure rises from 13 cm. at $-60°$ to 142 cm. at $+10°$. The boiling point at 760 mm. was found to be $-5·5°$. A series of thermochemical data are given of the formation of nitrosyl chloride from its elements, and other reactions.

Group VI.

Some attention has been paid to the action of sulphur trioxide on various compounds. For example, when molten sulphur trioxide and silicon tetrachloride are mixed, a slow reaction sets in; at a temperature of 50° the reaction is complete in from six to ten hours.[74]. It takes place according to the following equation:

$$2SiCl_4 + 2SO_3 = Si_2OCl_6 + S_2O_5Cl_2;$$

with a large excess of sulphur trioxide a second reaction takes place: $Si_2OCl_6 + 6SO_3 = 2SiO_2 + 3S_2O_5Cl_2$. Silicophosgen is not formed.

The action of sulphur trioxide on certain salts of sodium, potassium, and ammonium has also been studied.[75] A weighed quantity of the salt was placed in a specially devised desiccator which contained sulphuric acid, and the apparatus was then

[70] *T.*, 1893, **63**, 1089.

[71] *Zeitsch. Elektrochem.*, 1906, **12**, 513; *A.*, 1906, ii, 655.

[72] *J. Chim. phys.*, 1909, **7**, 169; *A.*, 1909, ii, 479.

[73] *Zeitsch. Elektrochem.*, 1908 **14**, 713; *A.*, 1908, ii, 1014.

[74] C. R. Sanger and E. R. Riegel, *Zeitsch. anorg. Chem.*, 1913, **80**, 252; *A.*, ii, 405.

[75] W. Traube, *Ber.*, 1918, **46**, 2513, 2525; *A.*, ii, 947.

exhausted. In this way all traces of moisture were removed from the salt and from the walls of the apparatus. The sulphuric acid was then removed and replaced by fuming sulphuric acid, and the apparatus once more exhausted. The various salts were left for several days exposed to the sulphur trioxide vapour. All the sulphur trioxide was carefully removed from the apparatus before the compounds were brought into the air. The increase in weight of the salts was determined, and they were also analysed. In the case of the chlorides two molecules of sulphur trioxide were absorbed by one molecule of the salt with the production of the chloropyrosulphonate, for example, $ONa{\cdot}SO_2{\cdot}O{\cdot}SO_2Cl$. In the case of sodium nitrite one molecule takes up three molecules of sulphur trioxide to give the nitrosotrisulphonate, $NO_2(SO_3)_3Na$, a salt that reacts violently with water with evolution of oxides of nitrogen.

Sodium and potassium persulphates give perpyrosulphates according to the equation $K_2S_2O_8 + 2SO_3 = KS_2O_6{\cdot}O_2{\cdot}S_2O_6K$. These perpyrosulphates deliquesce in air without the evolution of oxygen, and the solution thus obtained contains hydrogen peroxide and persulphuric acid in varying proportions. When placed direct into water they dissolve with violent hissing, and give off ozonised oxygen. The solution then only contains traces of hydrogen peroxide and persulphuric acid.

In the case of the fluorides only one molecule of sulphur trioxide is absorbed with the formation of the fluorosulphonate, for example, FSO_3Na, which can readily be dissolved from the insoluble fluorides by extraction with alcohol. Ammonium fluorosulphonate is easily prepared as a stable salt, and can be recrystallised from hot water in the form of needles, which melt at 245°. The fluorosulphonates are obtained also by heating together the dry fluoride and pyrosulphate. If ammonium fluoride is heated with fuming sulphuric acid, fluorosulphonic acid distils over in good yield. The fluorosulphonates are neutral to litmus. When the sodium salt is heated in an atmosphere of carbon dioxide, a gas is evolved which is probably sulphuryl fluoride, produced according to the equation: $2FSO_3Na = Na_2SO_4 + SO_2F_2$.

Some double compounds of hydrazine and chromous salts have been described.[76] Chromous acetate is suspended in air-free water, which is then covered with a layer of light petroleum; exactly the necessary quantity of acid is added to dissolve the salt, and a solution of hydrazine hydrate or hydrazine sulphate is then added, when the double salts are precipitated. For example, $CrCl_2 2N_2H_4$ and $CrBr_2 2N_2H_4$ were prepared, in the form of lilac powders. The salts generally are fairly stable.

[76] W. Traube and W. Passarge, *Ber.*, 1913, **46**, 1505; *A.*, ii, 604.

An exhaustive study has been made of the metallic tellurites.[77] In the case of the alkali metals, mono-, di-, and tetra-tellurites have been prepared. The first two are obtained by fusing tellurium dioxide with the calculated quantity of alkali carbonate, the last by the action of water on the ditellurites. In the case of other metals, the tellurites are prepared by the action of sodium tellurite on a soluble salt, usually the chloride. The alkali metal salts are soluble in water, those of the alkaline earth metals are sparingly soluble, whilst the salts of the heavy metals are insoluble. They are all somewhat unstable, being decomposed by carbon dioxide, and when heated in air to 440° to 470° they are oxidised. The following compounds were studied: $K_2TeO_3,3H_2O$; $K_2Te_2O_5$; $K_2Te_4O_9,4H_2O$; $Na_2TeO_3,5H_2O$; $Na_2Te_2O_5$; $Na_2Te_4O_9,4H_2O$; $5MgTeO_3,9H_2O$; $3CdTeO_3,2H_2O$; Ag_2TeO_3; $NiTeO_3,2H_2O$; $CoTeO_3,H_2O$; and $3PbTeO_3,2H_2O$.

Group VII.

If a freshly prepared solution of sodium or potassium hypobromite is heated at 80° for a few minutes and then cooled and treated with an excess of ammonium chloride, it still retains oxidising power towards alkali arsenite.[78] The amount of oxidising power is about one-tenth of that of the original solution. It was analytically proved that the solution contains sodium or potassium bromite. It was also found that in the spontaneous change of hypochlorite or hypobromite solution into chlorate or bromate the chlorite or bromite exists as a definite intermediate phase. These salts were found to exist in solutions of hypochlorites and hypobromites which had been kept for a considerable length of time. The view has been put forward that the first stage in the reaction is the formation of the chlorite or bromite, and that this is then oxidised by a further quantity of hypochlorite or hypobromite to the chlorate or bromate.

Group VIII.

By the action of fluorine on metallic osmium heated in a platinum tube, OsF_4, OsF_6, and OsF_8 have been prepared.[79] The octafluoride can readily be separated from the others by exhausting the tube, and condensing the compound in a vessel cooled by liquid air. It forms yellow crystals, melting at 34·5°. The osmium was

[77] V. Lenher and E. Wolesensky, *J. Amer. Chem. Soc.*, 1913, **35**, 718; *A.*, ii, 582.
[78] J. Clarens, *Compt. rend.*, 1913, **156**, 1998; **157**, 216; *A.*, ii, 693, 772.
[79] O. Ruff and F. W. Tschirch, *Ber.*, 1913, **46**, 929; *A.*, ii, 416.

prepared from the dioxide by very careful reduction in an atmosphere of hydrogen and carbon dioxide. From one gram of metal about 0·6 gram of OsF_8 was prepared. A series of vapour density measurements showed conclusively that it has a formula OsF_8, and in this way the octavalence of osmium is clearly established.

E. C. C. Baly.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

The subdivision into three parts of the section of the Annual Reports dealing with Organic Chemistry has naturally simplified the work of the reviewers considerably, but has restricted the opportunities to make a general survey of the developments in this branch of the subject. It would be unfortunate if the change of policy, desirable in itself, had the effect of banishing from the pages of the Reports those critical reviews, embracing the whole field of organic research, which have in the past been conspicuous and useful features of this section. In the meantime, however, there is little necessity to make provision for a general introduction, as the accounts given in previous volumes of the tendencies and principles which appear to be operative in organic research can be applied equally well to the position of Organic Chemistry at the present time.

A survey of the investigations in the aliphatic series published during the past eighteen months fails to find any one particular discovery which can be ranked as of outstanding importance, or as likely to produce revolutionary changes in our ideas. Dramatic discoveries are fortunately rare in organic chemistry, and even the most important observations may pass unnoticed, through lack of the necessary perspective, when records of research are compiled annually. It is nevertheless evident that original work in the aliphatic series continues to be of a high quality, although, in many ways, it is more restricted in scope than was formerly the case. In several classes of compounds little or no progress has been made, and research shows a distinct tendency to concentrate on a comparatively limited number of specific problems. To a certain extent, particularly in the remarkable developments which have recently been noticeable in the chemistry of hydrocarbons and reactions involving catalysis, this result is largely due to the pressure of technical influences, but at the same time the effect of other controlling forces is apparent. The renewed interest in biological problems has undoubtedly stimulated research in the

aliphatic series, and the rapid progress now being made in synthetical reactions promoted by enzymes may be quoted as a conspicuous but by no means unique example of this, but it is equally evident that the application of physical methods to the constitutional problems of organic chemistry is the most significant feature of recent research. Papers of a purely descriptive nature are now less frequently encountered, and, as a necessary result, much of the work now being done has a definite object in view and is strictly continuous. There is still, however, a regrettable tendency in some quarters to publish results in small and apparently unconnected fragments, or to describe isolated syntheses without giving any idea of the ultimate object of the research.

With regard to the arrangement of the present Report, it need hardly be said that no attempt has been made to cover the whole ground, nor has the writer restricted himself to publications which have only appeared during the past year. As far as possible, attention has been directed to work which has resulted in definite conclusions, but occasionally topics which are incompletely developed are discussed when the present position of the subject shows features of special interest. Owing to the fact that recent Presidential Addresses have dealt exhaustively with such broad theoretical questions as the Walden inversion and the relationship between constitution and optical activity, these subjects have been left practically unreviewed, so as to afford more space for other theoretical problems. Within limitations, the writer has not hesitated to devote special treatment to the subjects in which he is particularly interested, while keeping in the foreground the idea that the Report may appeal not only to the mature research worker, but may also be within the scope of the student who has reached that difficult stage in his career when text-books are insufficient and original literature too unwieldy or too difficult.

Hydrocarbons.

The vigorous research which has lately been applied to the problem of the synthesis of caoutchouc still continues to add materially to the bulk of the literature, and has doubtless conveyed a certain indirect stimulus to the study of hydrocarbons generally. It must, however, be confessed that, with the exception of work with a technical aspect, comparatively few researches on aliphatic hydrocarbons can be viewed as being, in the best sense, systematic and continuous; the exceptions to the above statement are consequently invested with a special interest.

Further evidence bearing on the vexed question of the origin of natural paraffins is being gradually accumulated as the indirect

result of various investigations. For example, in the last two or three years, it has been shown that the catalytic formation of methane and other hydrocarbons can be brought about by a large variety of metals which in some cases appear to act simultaneously as oxidation and reduction catalysts, and viewing these results as a whole, support is lent to the idea that processes of a similar kind are, in all probability, operative in nature. These catalytic reactions will be referred to in detail in a subsequent section, and, in the meantime, attention may be directed to another point. The optical activity observed in certain natural paraffins does not of necessity imply the existence, in the specimen, of active hydrocarbons of the paraffin series, and the caution with which such observations must be regarded is again emphasised by the results obtained in an examination of a technical sample of liquid paraffin.[1] The dextrorotatory constituents of the specimen were found to accumulate in the portions of higher boiling point, and these, on treatment with nitric acid, became quite inactive. As optically active hydrocarbons of the paraffin series are not affected by this reagent, the conclusion is drawn that the original activity was due to the presence of polynaphthenes. This is by no means an isolated observation, as other workers have obtained similar results, and it is evident that further research on this important problem is necessary before even superficial generalisations can be made as to the origin of natural paraffins.

Before leaving the subject of saturated hydrocarbons, attention may perhaps be drawn to a convenient method of preparing pure methane.[2] The process consists in decomposing aluminium carbide with water, and, after absorption of acetylene in the usual manner, the free hydrogen is removed by direct union with oxygen. The product, as finally purified, was shown to be free from both hydrogen and oxygen, and, considering the importance of pure methane as a test substance in researches on the mechanism of combustion, the method will doubtless find many applications.

With the exception of papers of a purely technical nature, comparatively few publications have recently dealt with unsaturated hydrocarbons, but the question of the structure of halogen substitution products of acetylene has been re-opened by Biltz, who expresses concern that Nef's ideas regarding the nature of these compounds should pass into the permanent literature without more definite proof.[3] A number of arguments are submitted in favour of the view that dihalogen derivatives of acetylene are to be

[1] J. Marcusson and C. Vielitz, *Chem. Zeit.*, 1913, **37**, 550; *A.*, i, 581.
[2] C. Campbell and A. Parker, *T.*, 1913, **103**, 1292.
[3] *Ber.*, 1913, **46**, 143; *A.*, i, 241.

regarded as constituted according to the simple structure CX:CX, and many objections are offered to Nef's alternative formulæ, $CX_2{:}C>$ and $CX_2{:}C<$. The paper gives a summary of the somewhat unexpected reactions of these compounds which may prove useful. Several other publications have been concerned with the nature of the compounds formed by the union of acetylene with various metallic salts, but, naturally enough, the evidence regarding the structure of these substances is somewhat scanty, and no useful purpose would be served by discussing the results in detail.

An example of the synthesis of an acetylenic hydrocarbon, through the agency of diquaternary ammonium bases, is instructive as furnishing a convenient method of increasing the unsaturation of a hydrocarbon.[4] Starting from the dibromide of butadiene, $\alpha\delta$-tetramethyldiamino-Δ^{β}-butylene, $NMe_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}NMe_2$, was obtained by the action of dimethylamine. The corresponding diquaternary ammonium base, when heated under diminished pressure according to the modern method of conducting such decompositions, yielded vinylacetylene, $CH{:}C{\cdot}CH{:}CH_2$, as the essential product. The distribution of valencies in a compound of this description offers many possibilities for research, but, as the boiling point of the hydrocarbon is low, the experimental difficulties likely to be encountered may limit its examination in greater detail.

Caoutchouc.—Much ingenuity continues to be expended on the problem of preparing isoprene and similar hydrocarbons, and the references on this topic to be found in the patent literature are no less numerous than last year. Little would be gained by any attempt to systematise these methods, as no process seems too improbable to merit publication or registration. There is, however, a growing tendency to fall back on methods which depend on catalysis for the preparation of unsaturated hydrocarbons generally, and doubtless in this direction lies the successful reaction to the discovery of which so much research is being devoted. On the other hand, considerable progress had been made in attempts to gain an insight into the nature of the caoutchouc complex, and the main result is the identification of an eight-carbon ring as the essential part of the structure.

By saturation of a chloroform solution of natural caoutchouc with hydrogen chloride, bromide, or iodide, definite addition products corresponding with the formula $C_{10}H_{16},2HX$ can be precipitated by the addition of alcohol.[5] It is pointed out in the original paper that, although similar products are obtained from

[4] R. Willstätter and T. Wirth, *Ber.*, 1913, **46**, 535; *A.*, i, 330.

[5] C. D. Harries, *ibid.*, 733; *A.*, i, 380.

caoutchouc prepared from isoprene, the additive compound with hydrogen iodide contains only one molecule of the halogen acid. At the same time, it would appear that the dihydriodide is formed only with difficulty, as in a parallel research on natural caoutchouc, in which similar methods were used, only the monohydriodide, $C_{10}H_{16}$,HI, was isolated.[6] The halogen hydride present in these additive compounds may be removed by the action of pyridine, and the products thus obtained are not identical with natural caoutchouc, but resemble the substance prepared from isoprene through the agency of sodium. If, however, the removal of the halogen acid is effected by treatment with alkalis, an entirely different form of caoutchouc is formed. In view of the fact that these "regenerated caoutchoucs" react imperfectly with ozone, it has, in the meantime, been suggested that their molecules include a conjugated system of double linkings, and the following formulæ have been proposed:

$$CHMe\begin{<}CH_2\cdot CH_2\cdot CH_2\\ CH{=}CH{-}CH\end{>}CMe \qquad\qquad CHMe\begin{<}CH_2{-}CH{=}CH\\ CH_2\cdot CH_2\cdot CH\end{>}CMe.$$

It is important to notice that the above structures are based on the idea that caoutchouc, and substances of a similar nature, are derived from eight-carbon rings. Harries, who has recently devoted considerable attention to this aspect of the structural question, has compared the velocity of decomposition of the ozonide of "normal" butadiene-caoutchouc with that derived from $\Delta^{1:5}$-*cyclo*octadiene. Both compounds were found to decompose at the same rate to give practically identical amounts of succindialdehyde. As Harries has repeatedly shown, the decomposition curves of ozonides constitute excellent standards of comparison, and the reasonable conclusion from the experiment just mentioned is that the caoutchouc complex is an aggregate of eight-carbon rings.[7] Additional evidence of a more direct nature was obtained from a series of reactions in which caoutchouc, regenerated from the hydrochloride, was converted into the ozonide, which was heated with water at 125°. Several products were thus obtained, notably levulinaldehyde and *cyclo*octane-1 : 5-dione, and the following interpretation of these changes is suggested:

$$\left[CMe\begin{<}CH_2\cdot CH_2\cdot CH\\ CH\cdot CH_2\cdot CH_2\end{>}CMe\right]_x \longrightarrow$$

Natural caoutchouc.

$$\left[CH_2{:}C\begin{<}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{>}C{:}CH_2\right]_n \longrightarrow CO\begin{<}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{>}CO$$

One form of regenerated caoutchouc.

[6] F. W. Hinrichsen, H. Quensell, and E. Kindscher, *Ber.*, 1913, **46**, 1283; *A.*, i, 637.

[7] C. D. Harries, *Annalen*, 1913, **395**, 211; *A.*, i, 284.

One feature of the paper now under review is the claim, based on the comparison of the decomposition curves of ozonides, that "sodium" caoutchouc derived from both isoprene and butadiene sources is essentially different in structure from the natural compound.

Needless to say, many investigations continue to deal with such problems as vulcanisation and the direct addition of oxygen to caoutchouc, and the recent recognition of the part played by the nitrogenous constituents has also received considerable attention, but the progress made in these inquiries does not call for special mention.

Alcohols, Aldehydes, and Ketones.

With one notable exception, few investigations of the past year have dealt exclusively with alcohols of simple structure. The exception referred to is the preparation of a large number of optically active alcohols of the type Et·CH(OH)·R, and although, for reasons stated in the introduction, it is not proposed on the present occasion to discuss optical results, the latest contribution to this important and well-developed series of investigations should not pass unmentioned.[8]

In last year's Report reference was made to the success which has attended the efforts of Wohl and his pupils in the synthesis of dialdehydes, and it was pointed out that work with compounds of this nature is greatly hampered by their tendency to polymerise. It may be noted that this change has in many cases been traced to the presence of moisture.[9] Thus, on distilling glyoxal which had been dried over phosphoric oxide at 95°, the unimolecular compound was obtained, and this is in agreement with a similar result obtained by Meisenheimer in the case of methylglyoxal.[10]

A somewhat drastic, but apparently efficient, method for reducing aliphatic aldehydes and ketones to the corresponding hydrocarbons depends on the action of amalgamated zinc in presence of concentrated hydrochloric acid.[11] The process has been applied successfully to heptaldehyde, which gives a good yield of *n*-heptane, and even better results have been obtained with ketones, where, in some cases, the yields are practically quantitative. As the reaction appears to be superior in many respects to that in which sodium and absolute alcohol are employed, its applications should be both numerous and important.

The reactions of β-ketonic esters continue to yield interesting

[8] R. H. Pickard and J. Kenyon, *T.*, 1913, **103**, 1923.
[9] C. D. Harries, *Ber.*, 1913, **46**, 294; *A.*, i, 342.
[10] J. Meisenheimer, *ibid.*, 1912, **45**, 2635; *A.*, 1912, i, 831.
[11] E. Clemmensen, *ibid.*, 1913, **46**, 1837; *A.*, i, 733.

results, and a new method has been described for preparing these compounds by a modification of Reformatski's reaction. Thus, the action of amalgamated zinc on a mixture of ethyl ethoxyacetate and ethyl bromoacetate resulted in the formation of ethyl γ-ethoxyacetoacetate, and a number of more complex examples are quoted in the original paper.[12] In this connexion, it may be noted that a recent study of the decomposition of β-ketonic esters shows that certain of these compounds, when heated at 200° with a small proportion of water, undergo ketonic decomposition in practically a quantitative manner.[13] It is significant that only those β-ketonic esters which are capable of undergoing enolisation can participate in the reaction, and this excludes the suggestion that the process depends simply on the hydrolysis of the ester and the subsequent elimination of carbon dioxide. Apparently the facility of the decomposition varies directly with the tendency of the ketonic ester to enolise. The suggestion is made that the reactions proceed according to the general scheme:

$$R\cdot CO\cdot CH_2\cdot CO_2R' \longrightarrow R\cdot CO\cdot CH{:}C(OH)\cdot OR' \xrightarrow{H_2O} R\cdot CO\cdot CH_3 + CO_2 + R'\cdot OH,$$

and in the original paper some results are quoted in support of this view.

Another interesting series of reactions which throw light on the enolisation of simply constituted ketones is described by Favorski.[14] By the action of phosphorus pentachloride on di*iso*propyl ketone, he finds that the customary replacement of the carbonylic oxygen by two atoms of chlorine only takes place to a limited extent, and the main product of the reaction is *iso*propyl α-chloro*iso*propyl ketone, $CMe_2Cl\cdot CO\cdot CHMe_2$.

Moreover, products of the above type are invariably produced by the action of phosphorus pentabromide. The nature of the reaction which ensues when a ketone is acted on by a phosphorus haloid would thus appear to depend on the capacity of the ketone to undergo enolisation. When the normal ketonic structure persists, two halogen atoms are introduced into the carbonyl group, and, on the other hand, when the conditions employed are favourable to enolisation, the following scheme represents the sequence of changes:

$$CHR_2\cdot CO\cdot CHR_2 \longrightarrow CR_2{:}C(OH)\cdot CHR_2 \longrightarrow CR_2Cl\cdot CO\cdot CHR_2.$$

The generalisations made in the original paper are based on a praiseworthy number of experimental results.

[12] T. B. Johnson, *J. Amer. Chem. Soc.*, 1913, **35**, 582; *A.*, i, 587.
[13] H. Meerwein, *Annalen*, 1913, **398**, 242; *A.*, i, 858.
[14] A. E. Favorski, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1339; *A.*, i, 12.

A variation of Knorr's method of synthesising pyrrole derivatives is involved in the condensation of amino-ketones with esters of β-ketonic acids in alkaline solution,[15] and a simplification of the process consists in the replacement of the ketonic esters by ketones. In this way, acetone and aminoacetone react to give 2 : 4-dimethylpyrrole, and a similar result has been obtained by the interaction of aminoacetone and ethyl oxalacetate.

The use of sodamide, in conjunction with alkyl iodides, as an alkylating agent has been extended to aliphatic ketones, and although the process was in the first instance applied to cases, such as pinacoline, where a tertiary carbon atom is attached to the carbonyl group, it seems to be capable of general application.[16] As a typical example, the action of the alkylating agent on diethyl ketone may be given. The products in this case consisted essentially of ethyl *iso*propyl ketone and di*iso*propyl ketone, thus indicating that the reagent had affected successive substitution on either side of the ketonic group. A property which seems to be characteristic of alkylated ketones, and which may be noted, is their failure to form oximes or other similar derivatives. Another method of alkylation, originally designed for cyclic ketones, has now been shown to be also applicable to certain aliphatic compounds.[17] The process, which has been developed by Kötz and Blendermann, consists in condensing the ketone with ethyl oxalate, heating the sodium derivative of the ketonic ester thus produced with an alkyl haloid, and finally hydrolysing with alkali hydroxides. In the meantime it is perhaps premature to claim the method as one of general application in the aliphatic series, but, from the experimental point of view, it evidently possesses many advantages.

As is well known, the use of acetone as a solvent and a reagent is greatly influenced by the presence of impurities, and an economical method of purifying the commercial product will be welcomed. The fact that sodium iodide unites with acetone to give a crystalline compound, $NaI,3C_3H_6O$, has now been applied to the purification of the ketone on the laboratory scale, and inspection of the working details given in the original paper[18] shows that the method is both convenient and efficacious.

Tautomerism.

During the past three or four years the experimental study of tautomeric phenomena has been greatly extended, and previous

[15] O. Piloty and P. Hirsch, *Annalen*, 1913, **395**, 63 ; *A.*, **i**, 292.
[16] A. Haller and E. Bauer, *Ann. Chim. Phys.*, 1913, [viii], **29**, 313 ; *A.*, i, 829.
[17] A. Kötz and K. Blendermann, *J. pr. Chem.*, 1913, [ii], **88**, 257 ; *A.*, i, 1069.
[18] Miss K. Shipsey and E. A. Werner, *T.*, 1913, **103**, 1255.

Reports contain copious references to the more recent developments in this field. At the present time, comparatively few compounds of a purely aliphatic nature appear to be employed in extending our ideas of the keto $\rightleftharpoons$enol transformation, and the subject thus falls naturally within the compass of another section of the Reports.

Special attention should be drawn, however, to a paper dealing with the more recent results obtained by Meyer in his systematic study of tautomeric change, as, apart from the new experimental results described, the author makes a number of useful suggestions which may serve to simplify the nomenclature which has crept into use in referring to different types of tautomeric compounds.[19] He also weighs once more the claims of existing theories of desmotropic reactions, and again comes to the general conclusions that the additive theory is probably correct, and that the enolic variety is the more reactive form. Despite the accumulation of evidence that, in certain changes, such as bromination, reaction proceeds through the enolic form, rigid generalisations on this point cannot yet be made. An interesting result bearing on this aspect of the keto-enol question has arisen, presumably as a side issue, in the synthesis of optically active spirans carried out by Leuchs.[20] Starting with optically active 1-hydrindone-2-benzyl-*o*-carboxylic acid, he obtained an active product after bromination and subsequent action of alkali. The conclusion is drawn that the bromination of the original acid must have taken place to a certain extent directly and without preliminary enolisation of the keto-group, as, otherwise, the asymmetry would be destroyed in the process, and the final product would have necessarily been inactive. This isolated result is not in itself conclusive, and may be explained on the assumption that the ketonic acid is associated to some extent, in which case the series of reactions can be regarded as involving a "partial asymmetric synthesis."[21]

Other work which bears on the application of the addition theory has shown that not only does hydrogen bromide convert acetyl chloride into acetyl bromide, but that the converse reaction, brought about by hydrogen chloride, results in the formation of acetyl chloride from the bromide.[22] The idea is again put forward that this result can be best explained by the supposition that in each case the additive compound $CH_3{\cdot}C(OH)BrCl$ is formed, and this may part with either hydrogen chloride or bromide, according to the conditions. Extending this explanation to the bromination

[19] K. H. Meyer, *Annalen*, 1913, **398**, 49 ; *A.*, i, 704.

[20] H. Leuchs, *Ber.*, 1913, **46**, 2435 ; *A.*, i, 974.

[21] A. Lapworth, *P.*, 1913, **29**, 289.

[22] O. Aschan, *Ber.*, 1913, **46**, 2162 ; *A.*, i, 820 ; H. Staudinger and E. Anthes, *Ber.*, 1913, **46**, 1417 ; *A.*, i, 616.

of acid chlorides, it will be seen that the same intermediate compound will result, irrespective of the route followed by the reaction:

(I) *Bromination by substitution:*

$$CH_3{\cdot}COCl + Br_2 \longrightarrow CH_2Br{\cdot}COCl + HBr \longrightarrow CH_2Br{\cdot}CClBr{\cdot}OH.$$

(II) *Bromination by addition:*

$$CH_3{\cdot}COCl \longrightarrow CH_2{:}C(OH)Cl \longrightarrow CH_2Br{\cdot}CClBr{\cdot}OH.$$

The results of this research do not materially affect the position of the addition theory, and certainly dispose of the objections to it raised in a paper describing the formation of butyryl bromide from butyryl chloride by the action of hydrogen bromide.[23]

A new departure in the experimental treatment of tautomeric change, which may prove useful in the future, is marked by the adoption of ozone as a reagent.[24] The advantages of the process lie in the facts that the addition to the enolic form proceeds at low temperatures, and apparently without inducing structural alterations in the substance under examination. As a specific example, a chloroform solution of benzoylacetone was treated with ozone, and the ozonide decomposed with water. The products consisted of benzoic acid in almost quantitative amount, together with methylglyoxal, which was isolated in the form of the osazone. Direct evidence is thus obtained pointing to the fact that, out of six possibilities, benzoylacetone is, under the conditions of the experiment, enolised according to the formula:

$$OH{\cdot}CPh{:}CH{\cdot}CO{\cdot}CH_3.$$

The same result has already been indicated by observations of the magnetic rotatory power of chloroform solutions. Other examples of the application of ozone are furnished by oxalacetone and ethyl acetoacetate. In the former case, a yield of 93·5 per cent. of oxalic acid was obtained on decomposing the ozonide, from which it would appear that the enolisation had also involved the acetyl group to some extent. The ozonide of ethyl acetoacetate was produced only in small amount, and the products of molecular rupture corresponded with those to be expected from the enolic modification. Unfortunately, although it is stated in the original paper that the specimen of ethyl acetoacetate was enolised to the extent of about 8 per cent., no details are given as to the yield of ethyl phenylhydrazoneglyoxylate. This is probably unavoidable in view of the small scale in which such experiments are carried out, but further information on this point is of evident importance, in view of the claim that the reaction with ozone does not affect the proportions of the two forms, and is confined to the enolic variety.

[23] A. Michael and E. Scharf, *Ber.*, 1913, **46**, 135; *A.*, i, 246.

[24] J. Scheiber and P. Herold, *ibid.*, 1105; *A.*, i, 490.

Excluding processes depending on the use of optically active solvents, polarimetric methods of studying the keto-enol change must of necessity be of limited application and suffer from several restrictions. Evidently when the labile hydrogen atom is linked to the asymmetric carbon atom, one factor necessary for quantitative work of this description is the independent existence of an active modification of the ketonic form. On the other hand, in the special case of acids, it is possible to trace the tautomeric changes by polarimetric observations on optically active derivatives, such as esters, and an interesting study of this nature is reported.

l-Menthyl *d*-phenylacetoacetate exists in the solid state as the ketonic modification, and is initially dextrorotatory in benzene solution. The activity gradually alters to lævorotatory, and ultimately the permanent rotation is entirely due to the presence of the *l*-menthyl group. The velocity of the change varies greatly, and, as in other similar cases, this can be attributed to the action of alkaline catalysts, and several instructive examples are quoted showing the effect of piperidine in promoting the change, even when the mutarotation remains under ordinary conditions completely suspended.[25]

From a spectroscopic examination of various substances containing labile hydrogen atoms, it has been shown, in the case of compounds which give only general absorption in alcoholic solution but display banded absorption in the presence of alkali, that the persistence of the bands depends on the amount of alkali present.[26] This result is in agreement with that arrived at by Hantzsch in similar work on ethyl acetoacetate, and, in view of the number and nature of the compounds now examined, would appear to be general. The evidence accumulated in this and similar investigations supports the conclusion that the bands are the spectra of alkali salts derived from the grouping $\cdot CO \cdot CH_2 \cdot CO \cdot$, but it should be noted that the existence of bands is limited to cases where the formation of internal complex salts seems probable. Incidentally, as a side issue of the general investigation, it was ascertained that spectroscopic evidence is opposed to the idea that a disodium compound of ethylmalonate exists.[27]

Catalysis.

In previous Annual Reports, considerable space has been devoted to the subject of catalysis, and it is more than ever evident, at the present time, that researches on catalytic reactions are being

[25] H. Rupe and E. Lenzinger, *Annalen*, 1913, **398**, 372; *A.*, i, 884.
[26] P. J. Brannigan, A. K. Macbeth, and A. W. Stewart, *T.*, 1913, **103**, 406.
[27] A. K. Macbeth and A. W. Stewart, *P.*, 1913, **29**, 11.

prosecuted with a vigour which has seldom been surpassed in the history of organic chemistry. A scrutiny of the abstracts of papers published during the past ten or twelve years shows that this development has gradually been gaining strength, and it is significant that a large proportion of the researches under this heading are now described in the patent literature rather than in scientific publications. The past year has been unusually fruitful in the number of new applications of catalysis, and in the bewildering variety of catalytic agents which have been successfully employed.

Reduction.—Considering the fact that distinct schools of research are now associated with reactions involving catalytic reduction, it is not surprising to find that many important results of this nature have to be reviewed. Catalytic reductions naturally fall under two headings: (*a*) those conducted at high temperatures, the reduced product being generally removed by distillation; and (*b*) reductions carried out in the liquid state or in solution at moderate temperatures. Processes of the latter type, when available, are for many reasons to be preferred, and at the present time seem to engage most attention.

In an important paper describing the reduction of unsaturated aldehydes and ketones,[28] Ipatiev mentions that he failed to reduce β-methyl-β-ethylacraldehyde by Skita's process, and admits that the universal method for the hydrogenation of organic compounds is still to be found. His own process, in which reduction is effected by the joint action of finely divided nickel, or palladium, and hydrogen under pressure, continues nevertheless to give highly interesting results. A notable feature of the work is the steady increase of the pressures employed. Thus, under a hydrogen pressure of 116 atmospheres, and in the presence of palladium as catalyst, acetylacetone is reduced to amylene βδ-glycol,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3.$$

Under similar conditions, but substituting nickel for palladium, the action was incomplete, and the reduced product consisted of methyl *n*-propyl ketone. This is an unexpected result, and emphasises the fact that the action of nickel, when applied in this way, is somewhat irregular, the efficiency of the catalyst in some cases being inferior, and in others superior to that of palladium.

An interesting application of Ipatiev's method is found in the reduction of carbohydrates. Aqueous-alcoholic solutions of reducing sugars may be hydrogenated at 110° by the agency of palladium and under a hydrogen pressure of 100 atmospheres. In this way lævulose was reduced to *d*-mannitol, dextrose to *d*-sorbitol, whilst lactose gave dulcitol as the essential product.[29] Inspection

[28] *Ber.*, 1912, **45**, 3218; *A.*, i, 10. [29] *Loc. cit.*

of the experimental details shows that in the two first-mentioned cases the yields appear particularly good, and the result will be welcomed, as reduction methods and, incidentally, oxidation methods also, are not particularly numerous in the sugar group. Another useful application of the process consists in the conversion of cyclic ketones into the corresponding saturated hydrocarbons by the joint action of reduction and dehydration catalysts.[30] Reactions of this type belong to another section of the Reports, but are of general interest in indicating the possibilities attending the use of mixed catalysts.

From the experimental point of view, the method of hydrogenation now being developed by Skita and his co-workers is exceedingly simple, and has proved of great service. The special advantage of the process lies in the fact that the reduction proceeds at the ordinary temperature and under pressures which rarely exceed one atmosphere. It is thus, as a rule, possible, as with Paal's method, to follow the course of a reaction, and to arrest a reduction at intermediate stages if desired. A useful review[31] of the working details shows that the use of gum arabic may be applied, not only to the production of colloidal solutions of palladium, but also to the formation of palladous hydroxide in a colloidal condition. These colloidal hydroxide solutions seem well suited to certain specific reduction processes, and, although the paper referred to deals principally with the hydrogenation of cyclic compounds, the working details given are of a general nature. The efficiency of the process has been somewhat increased by taking advantage of the fact, previously established, that reduction takes place more readily in certain solvents than in others, and also by increasing the hydrogen pressure slightly.[32]

It would appear that in many cases the action of platinum black as a catalytic agent in hydrogenation is highly effective, and may be superior to finely-divided palladium.[33] Thus, acetylenic γ-glycols may be reduced in presence of platinum to the saturated glycol (I), together with the corresponding alcohol (II):

(I) $OH\cdot CRR'\cdot[CH_2]_2\cdot CRR'\cdot OH$. (II) $OH\cdot CRR'\cdot[CH_2]_2\cdot CHRR'$.

Curiously enough, the corresponding hydrocarbon is not formed as the ultimate reduction product.

The important problem of converting unsaturated fats and fatty acids into the related saturated compounds has been unusually prominent during the past year, and has been carefully studied

[30] V. N. Ipatiev, *Ber.*, 1912, **45**, 3205 ; *A.*, i, 65.
[31] A. Skita and W. A. Meyer, *ibid.*, 3579 ; *A.*, i, 53.
[32] *Ibid.*, 3589 ; *A.*, i, 54.
[33] G. Dupont, *Compt. rend.*, 1913, **156**, 1623 ; *A.*, i, 696.

in the laboratory, and elsewhere. A variation of the customary process, in which reduced nickel or other metal is used as the catalyst, is reported by Bedford and Erdmann, who find that nickel oxide is peculiarly effective.[34] Not only so, but the oxide possesses an additional advantage over the metal in that it is less readily affected by hydrogen sulphide. The mechanism of the process seems to depend on the conversion of the higher oxides into the suboxide, which forms a black colloidal suspension with the oil or fat.

Excluding the entries in technical or patent literature, it is evident that the number of publications dealing with Sabatier and Senderens' method of reduction are now less numerous than has lately been the case. Among recent publications may be noted an account of the behaviour of heptyl alcohol when reduced at 220° in the presence of nickel.[35] The products consisted of about 62 per cent. of *n*-hexane, 17 per cent. of a mixture of heptyl alcohol and the corresponding aldehyde, together with carbon monoxide. The complete results of the investigation go to show that the first stage in the reaction consists in the decomposition of the alcohol into heptaldehyde and hydrogen. The aldehyde is then converted into *n*-hexylene, which undergoes further reduction into *n*-hexane. The investigation deserves special mention in view of the systematic attempts which were made to trace the individual steps in the series of reactions.

Simple methods for synthesising methane by catalysis have, of course, been known for some time, and several investigations have now been devoted to elucidating the reactions involved in these processes. It would appear that the conversion of carbon monoxide and water into methane can be effected by a great variety of metals or oxides, but metallic nickel at 600° gives the best results. Apparently metallic iron, alumina, and silica act through the temporary formation of carbides, which are at once decomposed by the water vapour to give the hydrocarbon.[36] It may also be noted that Ipatiev has come to the opinion that the direct synthesis of methane from its elements, in the presence of metals, depends on the catalytic oxidation of the carbon by means of metallic oxides present as impurities. The carbon dioxide produced is then reduced catalytically to methane, so that the series of reactions depends on joint catalytic effects.[37]

Other Examples of Catalysis.—Methods of preparing ketones

[34] *J. pr. Chem.*, 1913, [ii], **87**, 425 ; *A.*, i, 701.
[35] J. Böeseken and G. H. van Senden, *Rec. trav. chim.*, 1913, **32**, 23 ; *A.*, i. 331.
[36] L. Vignon, *Compt. rend.*, 1913, **157**, 131 ; *A.*, i, 949.
[37] *J. pr. Chem.*, 1913, [ii], **87**, 479 ; *A.*, i, 693.

which depend on the catalytic action of metallic oxides or carbonates on organic acids are daily becoming more numerous, and Senderens, who has been associated with this development during the past four or five years, has lately published a useful summary of the abundant literature which has accumulated round the subject.[38] It has now been shown that precipitated calcium carbonate is a useful catalyst in this type of reaction, and, although not so effective as thorium oxide, it retains its activity even after it has become coated with carbonaceous products.[39] The yield of ketone obtained by this agency is, however, satisfactory only in the lower members of the aliphatic series, but even valeric acid gives a 32 per cent. yield of dibutyl ketone. In every case the acids may be replaced by their anhydrides, and the process is also applicable to the preparation of mixed ketones.

At the same time, thorium oxide, as a catalyst in the preparation of ketones, is evidently superior in its range of application to any other agent, and an instructive example of its value is given by Pickard and Kenyon in their most recent account of optically active alcohols.[40] A number of the carbinols resolved in the course of this important research (and also in the previous work of the same authors) were obtained by reduction of mixed ketones, and these, in turn, were prepared catalytically from the corresponding acids. One typical example may be quoted which shows the efficiency of the process. By passing a mixture of equal amounts of myristic and propionic acids over thoria heated to 420°, a 60 per cent. yield of ethyl *n*-tridecyl ketone was obtained, and this result speaks for itself sufficiently. Incidentally, it may be mentioned that the use of thorium oxide as a catalyst frequently gives irregular results, and it is difficult to preserve the conditions necessary for any particular action. An additional example of this uncertainty is quoted by Baskerville, who states that although he observed all the conditions laid down by Sabatier and Mailhe, he nevertheless failed to obtain ethyl ether by the action of pure thorium oxide on alcohol vapour at 250°.[41]

It has been known for some time that glucinum salts can be dissolved in various organic solvents, and this has now led to the discovery that the ordinary process of esterification is considerably accelerated by the addition of glucinum acetate or hydroxide.[42] Better results were obtained when the vapours of the acid and alcohol were led over glucinum oxide heated at 310°. The products

[38] *Ann. Chim. Phys.*, 1913, [viii], **28**, 243 ; *A.*, i, 342.

[39] P. Sabatier and A. Mailhe, *Compt. rend.*, 1913, **156**, 1730 ; *A.*, i, 700.

[40] *T.*, 1913, **103**, 1923.

[41] *J. Amer. Chem. Soc.*, 1913, **35**, 93 ; *A.*, i, 155.

[42] O. Hauser and A. Klotz, *Chem. Zeit.*, 1913, **37**, 146 ; *A.*, i, 246.

were obtained in satisfactory yield, and the catalyst may be readily recovered, but, at the same time, it is doubtful if the process is more convenient than methods depending on the catalytic agency of sulphuric acid, as these have now reached a high degree of efficiency.[43]

A rapid method of converting primary alkyl chlorides or bromides into the corresponding secondary isomerides may occasionally be useful, and it has been shown that the change may be brought about by distilling the haloids over thorium chloride heated at 250°, and leading the products over pumice stone at 200°.[44] The reaction seems to involve the temporary decomposition into ethylenic hydrocarbons and hydrogen chloride or bromide, the products afterwards recombining to give the isomeric haloids.

Catalytic methods of oxidation have not been specially prominent in the aliphatic series of late, but it may be mentioned that Senderens has been engaged on a study of the direct oxidation of alcohols as a necessary preliminary to the investigation of the effect of metals and metallic oxides in accelerating the change.[45] The results so far obtained have not been specially promising, but there is little reason to doubt that this revival of an old reaction will ultimately be developed on profitable lines.

Halogen Compounds.

Systematic subdivision of the subject-matter of the Report would be difficult to maintain if halogen compounds were treated rigidly as a class by themselves, and consequently most of the references to these compounds are to be found under other headings where synthetical processes are discussed. So far as these practical methods are concerned, no specially striking development has been noted. Alkyl and acyl haloids have found their customary applications; work with Grignard reagents has been as extensive as ever, but the reaction has now found a permanent place as a standard synthetical method, and there is no necessity to refer to the many modifications of the process.

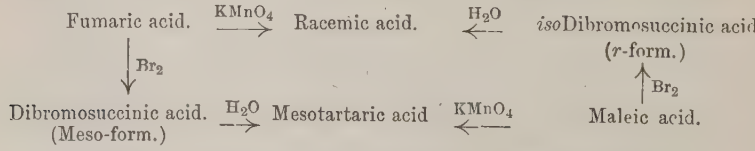
In several cases, however, researches on halogen compounds have dealt with structural problems, and many interesting results have been obtained. In the course of an examination of the optical properties of typical monobasic acids and their derivatives, the values found for the refractivity and dispersive power have been compared for the free acid, the ethyl ester, and the acid chloride.[46]

[43] F. Bodroux, *Compt. rend.*, 1913, **156**, 1079; *A.*, i, 440.
[44] P. Sabatier and A. Mailhe, *ibid.*, 658; *A.*, i, 330.
[45] J. B. Senderens, *ibid.*, 1909; *A.*, i, 814.
[46] K. von Auwers and M. Schmidt, *Ber.*, 1913, **46**, 457; *A.*, i, 338.

Practically without exception, the values could be arranged in the order: acid>chloride>ester; and extension of the determinations to the chlorides of the oxalic acid series has shown that succinyl and glutaryl chlorides must be regarded as possessing the normal symmetrical structure. This is in conformity with the results obtained during the past two years by other workers who have approached the problem by different methods. In the case of chlorides derived from unsaturated acids, the results are equally conclusive, and point to the fact that where the *trans*-configuration exists the resulting chloride is symmetrical. On the other hand, the optical values determined for chloromaleyl chloride clearly point to the structure $\begin{matrix}CH\cdot CCl_2\\ \|\\ CCl—CO\end{matrix}\!\!>O$. Although in general these conclusions are in good agreement with those arrived at by Ott,[47] it may be observed that the relative positions now ascribed to the halogen atoms are somewhat different from those previously suggested. It may be mentioned, in passing, that a further point of distinction between chlorofumaryl chloride and chloromaleyl chloride consists in the fact that the former resists the reducing effect of hydrogen and platinum black owing to paralysis of the catalyst. The observation is interesting, but it would be premature to claim this difference in behaviour as general in its nature or connected with symmetry of structure.

Acids and their Derivatives.

It is somewhat rare to encounter research work which finds immediate application in teaching, but many lecture courses will be affected by recent work on the isomeric dibromosuccinic acids. The relationship of these compounds with meso-tartaric and racemic acids has now to be regarded in a new light, as it has been shown that *iso*dibromosuccinic acid is a racemic form, and may be resolved into its active constituents.[48] The following scheme therefore represents the mutual relationships of the tartaric acids, the corresponding dibromo-acids, and the parent unsaturated acids:



Evidently the above transformations resemble those involved

[47] E. Ott, *Annalen*, 1912, **392**, 245; *A.*, 1912, i, 828.

[48] A. McKenzie, *T.*, 1912, **101**, 1196. See also P. F. Frankland, *T.*, 1912, **101**, 673.

in the Walden inversion, and two alternative explanations may be offered. The change of configuration may take place during the replacement of halogen by hydroxyl in the decomposition of the bromo-acids, or the addition of bromine atoms to the unsaturated acids may follow a different stereochemical course from the addition of hydroxyl groups by the action of permanganate. The available evidence is in favour of the latter alternative, and it appears likely that the change in configuration takes place during the addition of bromine.

Holmberg, who has also been engaged on problems similar to that outlined above, has shown [49] that the dichlorosuccinic anhydride obtained from maleic anhydride is a mixture of racemic and meso-forms in the proportion 5 : 1. This observation is evidently consistent with McKenzie's results, and it is highly significant that the change in configuration which accompanies the addition of halogen takes place while the anhydride structure remains intact. A further contribution to the stereochemistry of the halogen succinic acids shows that the formation of malic acid by the hydrolysis of sodium *l*-bromosuccinate probably takes place through the intermediate formation of propiolactonecarboxylic acid. The latter compound has been found to yield either *l*- or *d*-malic acid on hydrolysis, according as the change is effected in acid or alkaline solution, thus adding to the already numerous list of optical inversions encountered with these substances.[50]

The complicated problems connected with the chemistry of the glutaconic acids are one by one being solved as the result of systematic research. In last year's Report a complete account was given of the position then reached by Thorpe and his co-workers in their studies of the structural forms of glutaconic acid and its derivatives, and consequently it is unnecessary again to review the fundamental features of this line of inquiry. One of the points then left unsettled was the provision of experimental proof that the normal and labile forms of a glutaconic acid possess the *cis*-configuration. This has now been confirmed [51] by the reduction of the two forms of $\alpha\gamma$-dimethylglutaconic acid, a substance which is well adapted for this purpose. Hitherto only the normal form of the compound has been known, but the difficult task of isolating a labile modification from the corresponding hydroxy-anhydride has now been carried out, so that both varieties of the acid were available. After adjustment of the conditions of reduction, so as to ensure that the process would be unaccompanied by intra-

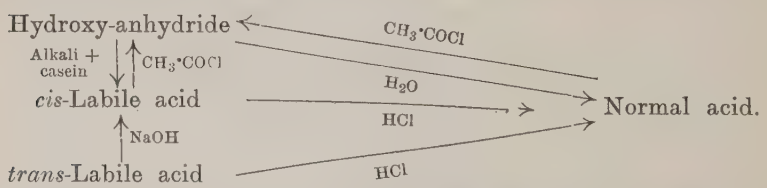
[49] B. Holmberg, *Svensk. Kem. Tid.*, 1912 ; *A.*, i, 7.
[50] B. Holmberg, *J. pr. Chem.*, 1913, [ii], **87**, 456 ; *A.*, i, 824.
[51] J. F. Thorpe and A. S. Wood, *T.*, 1913, **103**, 276.

molecular changes, it was found that each isomeride was converted into *cis*-dimethylglutaric acid.

Another result of more fundamental importance is the realisation of the idea, frequently emphasised in the course of these researches, that an acid of the glutaconic type should exist in three modifications.[52] The actual compound to furnish this result was β-phenyl-α-methylglutaconic acid, attention being directed to this example in view of the increased stability which follows the introduction of a molecularly heavy residue into the β-position, and the constitution assigned to the three isomerides is as shown below:

$CMe\cdot CO_2H$ $\|$ CPh $\|$ $CO_2H\cdot CH_2$	$\cdot CMe\cdot CO_2H$ $\|$ $CHPh$ $\|$ $\cdot CH\cdot CO_2H$	$CM\cdot CO_2H$ $\|$ CPh $\|$ $CH_2\cdot CO_2H$
trans-Labile acid.	Normal acid.	*cis*-Labile acid.

In the course of the synthesis of the acid, a mixture of the *cis*- and *trans*-forms of ethyl α-carbethoxy-β-phenyl-α-methylglutaconate was obtained, which boiled at a constant temperature. Fortunately, the *trans*-variety separated in the crystalline condition, and the isolation of the substituted glutaconic acid having the same configuration was thus rendered possible. The properties of the *trans*-labile acid are in complete harmony with the views expressed regarding its structure, and the mutual relationships of these interesting compounds may be summarised as follows:



Future work in this field will doubtless be aided by application of the convenient method of discriminating between the esters of the normal and labile acids.[53] The latter type of compound alone possesses the capacity to enter into condensation with ethyl sodiocyanoacetate, and, except in cases where the transformation of the normal into the labile ester occurs readily, the normal form fails to react. The process of alkylation of ethereal glutaconates, which takes place through the intermediate formation of a sodium derivative, is also governed by similar considerations, as alkyl derivatives are only formed from the labile modifications. Work in this direction is now so far advanced that it has been possible

[52] *T.*, 1913, **103**, 1569.

[53] J. F. Thorpe and A. S. Wood, *ibid.*, 1579.

to effect a series of generalisations on the whole process of alkylation, as applied to this type of compound.[54]

Under the heading of catalysis, special mention is made of catalytic methods of preparing aliphatic ketones, and it may be noted that similar methods may be employed to convert members of the succinic acid series into the corresponding cyclic ketones. In the meantime, the process has been confined to adipic acid, its homologues and substitution derivatives, and it has been found that a quantitative yield of *cyclo*pentanone may be obtained by heating adipic acid to 290° in the presence of barium hydroxide.[55] The reaction, which is carried out under diminished pressure and in an inert atmosphere, is evidently superior to the older methods of obtaining such compounds by the distillation of salts, and it is in many respects unfortunate that this discovery should have been so long delayed.

In an important paper by Scholl and Egerer, the question is revived as to the real nature of the oxalomalonic esters. Previous publications contain highly contradictory accounts of these compounds, particularly of the ethyl ester.[56] It has, however, now been proved that the compound obtained by Bouveault by the interaction of ethyl sodiomalonate and ethyl oxalic chloride, and described by him as triethyl oxalomalonate, is in reality ethyl oxalomethanetricarboxylate, $CO_2Et{\cdot}CO{\cdot}C(CO_2Et)_3$. Kurrein,[57] who carried out the same reaction in benzene solution, seems to have isolated merely a mixture of ethyl oxalate and malonate. Not only are a number of oxalomalonic esters fully described, but it has also been shown, in the paper referred to above, that, so long as alcohol is excluded, methanetricarboxylic esters may be employed for synthetic purposes in processes which resemble those depending on the use of ethyl sodioacetoacetate or sodiomalonate.

The applications of oxalyl chloride as a synthetic agent continue to be both numerous and important,[58] and, out of many examples of the use of this reagent, reference may be made to the synthesis of parabanic acid, together with a number of its derivatives.[59] As a rule, reaction between oxalyl chloride and carbamide takes place smoothly in ethereal solution, and in certain cases the yields obtained are excellent. This is particularly the case when doubly substituted carbamides are employed, and the reaction also applies, although imperfectly, to the preparation of thioparabanic acids.

[54] J. F. Thorpe and A. S. Wood, *T.*, 1913, **103**, 1752.

[55] D.R.-P. 256622 ; *A.*, i, 482.

[56] R. Scholl and W. Egerer, *Annalen*, 1913, **397**, 301 ; *A.*, i, 583.

[57] H. Kurrein, *Monatsh.*, 1905, **26**, 373 ; *A.*, 1905, i, 413.

[58] See *Chem. Weekblad*, 1913, **10**, 214 ; *A.*, i, 443, for a review of the literature since 1869.

[59] H. Biltz and E. Topp, *Ber.*, 1913, **46**, 1387 ; *A.*, i, 600.

The possibility that oxalic acid and hydroxy-acids may play a part in the natural production of carbohydrates has again been raised,[60] and, although little evidence of a positive nature is so far available, it may be noted that several methods are now known by means of which oxalic acid may be reduced to glycollic acid. Further, the latter compound undergoes decomposition into formaldehyde and formic acid under the influence of light, and these changes suggest a series of reactions by means of which the decomposition and the formation of sugars may be maintained as a cyclic process in the plant. Work in this field has not proceeded far, but the development of the subject will be closely watched.

Methods of obtaining anhydrides which depend on the use of sulphur chloride have been known for some time, and opinion has been divided as to the mechanism of such processes. An investigation bearing on this point has recently appeared,[61] where it has been shown that the action of the reagent on the silver salts of organic acids proceeds in two stages:

$$2R\cdot CO_2Ag + S_2Cl_2 \longrightarrow 2AgCl + (R\cdot CO_2)S_2.$$
$$2(R\cdot CO_2)S_2 \longrightarrow 2(R\cdot CO)_2O + SO_2 + 3S.$$

The anhydride ultimately produced thus results from the decomposition of an intermediate unstable compound, which may be regarded as an acyl thiosulphite. The reactions outlined above are not only interesting from the theoretical point of view, but form the basis of a good practical method for preparing anhydrides on the small scale. At the same time, the substitution of thionyl chloride for sulphur chloride gives a superior working method, and the reaction appears to be more general in its application, although the capacity to form definite intermediate compounds seems to be confined in this case to hydroxy-acids. Theoretically, the steps involved are:

$$2R\cdot CO_2Ag \longrightarrow (R\cdot CO_2)_2SO \longrightarrow (R\cdot CO)_2O + SO_2,$$

and, as the reactions proceed smoothly, the possibility is opened out of the preparation of normal anhydrides from hydroxy-acids. It would appear that this had already been realised in the case of glycollic and malic acids, and a definite step has thus been made towards evolving a general method for the preparation of compounds the isolation of which is either impossible or notoriously difficult.

It is perhaps important to point out that when thionyl chloride reacts with certain lactones the ring is ruptured and intermediate compounds containing both sulphur and chlorine are produced.[62]

[60] E. Baur, *Ber.*, 1913, **46**, 852; *A.*, i, 443.

[61] W. S. Denham and Miss H. Woodhouse, *T.*, 1913, **103**, 1861. See also *T.*, 1909, **95**, 1237.

[62] P. Barbier and R. Locquin, *Bull. Soc. chim.*, 1913, [iv], **13**, 223; *A.*, i, 336.

This certainly supports the idea expressed above that the formation of thionyl derivatives from hydroxy-acids involves the hydroxyl group.

Incidentally, it may be noted that the effect of thionyl chloride as a chlorinating reagent leads to variable results in the case of optically active compounds, save where a phenyl group is attached to the asymmetric carbon atom.[63] In other reactions, unconnected with optical activity, it has been found that many of the irregularities shown by thionyl chloride can be traced to the presence of impurities, and as these are generally substances which are prone to cause intramolecular changes, it is perhaps well to emphasise this point.[64]

Glycerol and Allied Compounds.

At the present time, the chemistry of glycerol is evidently passing through a stage when special attention is being directed to derivatives in which the hydroxyl groups are only partly substituted or are replaced by different substituents. Before discussing any new synthetical products obtained from glycerol, it may be well to refer back to results obtained a year ago in an examination of the freezing-point curves for binary mixtures of stearin, palmitin, and olein.[65] The results indicated the existence of a continuous series of solid solutions, and this is now claimed by Holde[66] as confirming his views that in olive oil the stearic and palmitic acids are not present as tristearin and tripalmitin, but as mixed glycerides.[67] It may, however, be noted that melting-point determinations in the case of such compounds are liable to be vitiated by a variety of circumstances. This is emphasised strongly by Grün, who has shown that anomalies in the consistency and melting point of fats may be due to the fact that certain glycerides may exist in two modifications, which although probably structurally identical, differ considerably in melting point.[68]

There is no doubt, however, that definite mixed glycerides do occur in solid fats, and Bömer now describes a new form of palmityldistearin,[69] which, together with a small proportion of stearyldipalmitin, was extracted from lard, and the same com-

[63] P. F. Frankland, *T.*, 1913, **103**, 720 ; A. McKenzie and G. W. Clough, *T.*, 1913, **103**, 687.

[64] H. Meyer and K. Schlegl, *Monatsh.*, 1913, **34**, 561 ; *A.*, i, 608 ; P. Barbier and R. Locquin, *Bull. Soc. chim.*, 1913, [iv], **13**, 229 ; *A.*, i, 337.

[65] R. Kremann and R. Schultz, *Monatsh.*, 1912, **33**, 1063 ; *A.*, 1912, ii, 1152.

[66] *Ber.*, 1912, **45**, 3701 ; *A.*, i, 158.

[67] *Ibid.*, 1902, **35**, 4306 ; *A.*, 1903, i, 140.

[68] *Ibid.*, 1912, **45**, 3691 ; *A.*, i, 157.

[69] A. Bömer, *Zeitsch. Nahr. Genussm.*, 1913, **25**, 321, 354 ; *A.*, i, 441, 442.

pounds have also been isolated from butter fat.[70] This line of inquiry has naturally stimulated the synthetical production of mixed glycerides, and, as a simple example of such work, mention may be made of the synthesis of α-myristo-β-stearin.[71] By the action of myristoyl chloride on glycerol-α-monochlorohydrin, the ester $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{13}H_{27}$ was obtained, and this, on treatment with stearoyl chloride, was converted into myristostearochlorohydrin, $CH_2Cl{\cdot}CH(O{\cdot}CO{\cdot}C_{17}H_{38}){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{13}H_{27}$. The final stage in the synthesis of α-myristo-β-stearin was accomplished by the action of silver nitrite, and obvious variations in the processes admit of the preparation of a large number of mixed glycerides.

An alternative method of obtaining an idea of the structure of the natural glycerides depends on the process of partial saponification of the compounds, and although sulphuric acid has hitherto been employed as the hydrolytic agent for this purpose, it has now been shown that alkali hydroxides are equally effective in displacing the fatty acid residues in definite stages.[72]

The use of substituted glycerols in pharmacology has in recent years been an important factor in directing the synthesis of simple derivatives of the trihydric alcohol. In this connexion it may be noted that the reaction between glycerol and phosphoric acid or phosphoric oxide is by no means so simple as would appear from the earlier publications on this topic, and, during the year, a number of fresh observations have been made, which do not, however, lead to any final conclusions on the subject. The claim made by Contardi that glycerotriphosphoric acid results from the action of 3 mols. of phosphoric acid on 1 mol. of glycerol is now contradicted by Carré,[73] and the lengthy dispute between these workers can apparently only be settled by approaching the problem by some entirely new route. Although at present the whole subject is in an incomplete state, it deserves reference in view of its importance.

Among derivatives of glycerol in which two hydroxyl groups are substituted, the compounds formed by condensation with aldehydes or ketones are of special interest. Glycerol benzylidene ether has now been obtained crystalline by heating glycerol and benzaldehyde in the absence of a catalyst.[74] The same method has furnished a trimethylene glycol benzylidene ether, and, what is more important from the structural point of view, propylene glycol also participates

[70] C. Amberger, *Zeitsch. Nahr. Genussm.*, 1913, **26**, 65; *A.*, i, 1040.
[71] A. Grün and B. Schreyer, *Ber.*, 1912, **45**, 3420; *A.*, i, 159.
[72] A. Lipp and P. Miller, *J. pr. Chem.*, 1913, [ii], **88**, 361; *A.*, i, 1038.
[73] *Compt. rend.*, 1912, **155**, 1520; *A.*, i, 156.
[74] W. Gerhardt, D.R.-P. 253083; *A.*, i, 47.

in a similar reaction. The condensation may therefore involve the hydroxyl groups attached to neighbouring carbon atoms.

Carbohydrates.

In the period under review, a large proportion of the researches in the sugar group have been concerned with the synthetic functions of enzymes, and the results obtained are of sufficient importance and variety to justify their treatment under a separate heading. At the same time, a considerable number of the publications of the past year have dealt with the application of ordinary synthetical processes to the sugars, and several highly interesting researches have to be noticed.

Special attention must be drawn to an investigation of fundamental importance in which the mechanism of acrose-formation is established with a considerable degree of certainty.[75] Fischer and Tafel, in their classical synthesis of α-acrose, isolated an isomeric substance (β-acrose), which in their opinion was allied to *dl*-sorbose. This conclusion has now been verified. By alkaline auto-condensation of pure glyceraldehyde, under conditions which would be unlikely to cause the aldose $\rightleftarrows$ ketose conversion, a solid, crystalline mixture of inactive hexoses has been obtained, from which *dl*-fructose was isolated by crystallisation from methyl alcohol. A more soluble constituent was also separated in the crystalline state, and this was proved to be *dl*-sorbose by comparison with an artificial mixture of the enantiomorphous forms. The identity was further confirmed by the preparation and examination of the corresponding osazones. Owing to the experimental advantages gained by working with definite solid compounds, several important points have been settled by the results of this investigation. The appearance of the ketonic group in the sugar synthesis must take place at the triose stage, and thus the reaction is not, strictly speaking, the auto-condensation of glyceraldehyde, but resolves itself into the condensation of glyceraldehyde with dihydroxyacetone. Limitations are thus imposed on the number of hexoses which can possibly be produced, and, in the original paper, it is shown on stereochemical grounds that the *dl*-varieties of fructose and sorbose should form the essential products.

Not the least striking feature of the work is the successful manipulation of small quantities of material, and the part played by external collaborators in confirming the conclusions.

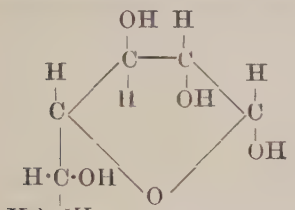
The more recent work of Fischer and Zach on the reactions of triacetyldibromoglucose has resulted in proving that the two halogen atoms in the compound are attached to the terminal

[75] E. Schmitz, *Ber.*, 1913, **46**, 2327 ; *A.*, i, 954.

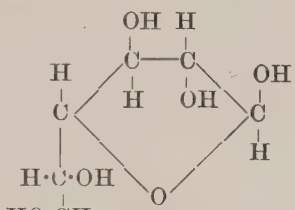
carbon atoms of the sugar chain, and this fact has led to the conversion of *d*-glucose into a methylpentose.[76] By the action of zinc dust and acetic acid on triacetylmethylglucoside bromohydrin,

$$CH_2Br\cdot CH(OAc)\cdot CH\cdot CH(OAc)\cdot CH(OAc)\cdot CH\cdot OMe$$
$$\qquad\qquad\qquad

determining the arrangement of hydroxyl groups in space is based on the well-known fact that orthoboric acid may be titrated in the presence of polyhydroxy-compounds.[79] It has now been shown that a pronounced exaltation in the conductivity of the acid is occasioned only by compounds containing at least one pair of hydroxyl groups, which are attached to neighbouring carbon atoms. Further, the maximum effects are obtained when the hydroxyl groups are situated on the same side of the carbon atoms, and lie in the same plane with them. One immediate result of the research is the allocation of definite configurations to α- and β-glucose. Of the two forms shown below, the compound possessing the configuration *A* should show a greater exaltation in the conductivity than *B*.



A.



B.

The two conductivity values should not, however, be permanent, as, owing to the interconversion of the sugars, one ought to diminish and the other increase until they coincide, when both forms of the sugar attain equilibrium in solution. These deductions were experimentally verified, and the configuration *A* thus ascribed to α-glucose. An important observation which strengthens the validity of the conclusions is that the velocity constants for the conductivity changes were identical with those determined for the simultaneous changes in rotation.

The investigation just referred to emphasises in a novel manner how the reactions of a sugar are influenced by the configuration of the hydroxyl groups, and this is also shown in the varying capacities of the sugars to form condensation compounds with aldehydes and ketones. Views similar to those formulated by Böeseken have also been expressed in connexion with the preparation of a series of partly methylated glucoses.[80] Incidentally, in the course of the latter work, evidence bearing on the application of Hudson's generalisation, regarding molecular rotations in the sugar group, has been gained by a study of the mutarotation displayed by dimethylglucose. Owing to the fact that the compound showed suspended mutarotation, it was possible to obtain

[79] J. Böeseken, *Ber.*, 1913, **46**, 2612; *A.*, i, 1147.

[80] J. C. Irvine and J. P. Scott, *T.*, 1913, **103**, 564, 575.

exact values for the specific rotations of the α- and β-forms, and these were found to agree closely with the figures required by Hudson's method of calculation. It may be remarked that the constitution assigned to dimethylglucose is still uncertain, in view of the conclusions recently arrived at by Macdonald in a careful study of the condensation of glucose with acetone.[81]

As the examination of natural products attracts numerous workers, a considerable number of new glucosides have been described during the year, but, generally speaking, there is no feature of these compounds which merits special attention in this section of the Report except that their varied composition emphasises the variety of substances which may exist in combination with the sugars. As an index of the high molecular magnitude of these natural glucosides, reference may be made to *caulosaponin* and *caulophyllosaponin*, to which the formulæ $C_{54}H_{88}O_{17}$ and $C_{66}H_{104}O_{17}$ have been respectively assigned.[82]

It is interesting to note that evidence is accumulating pointing to the fact that mannitol seems in many cases to be a fermentation product derived from trehalose, and its formation may be avoided by preserving plant extracts under sterilised conditions.[83] [84] The statement that mannitol is formed on drying certain sea-weeds[85] is not inconsistent with this view, as several years ago the writer had the opportunity of observing specimens of *Laminaria* which had become encrusted with mannitol after the cessation of active bacterial action on the surface of the thallus. In connexion with references to natural products, it may not be out of place to mention a short paper by E. O. von Lippmann[86] on the occurrence of trehalose and *d*-sorbitol, as, apart from the inherent interest of the observations, it is instructive to notice that the organic chemist on holiday may rival the biologist in the use he makes of his opportunities in the field.

Alkaloidal glucosides as a class are not numerous, and two examples of such compounds which have been recently synthesised may be referred to. By the use of acetobromoglucose in the standard method of synthesis, a definite morphine glucoside has been prepared,[87] and, in their work on bromotriacetylglucosamine, Irvine and Hynd isolated morphine glucosamine, which is the

[81] J. L. A. Macdonald, *T.*, 1913, **103**, 1896.
[82] F. B. Power and A. H. Salway, *ibid.*, 191.
[83] F. Busolt, *J. Landw.*, 1913, **61**, 153 ; *A.*, i, 803.
[84] *Ibid.*, 1912, **60**, 393 ; *A.*, i, 235.
[85] H. Kylin, *Zeitsch. physiol. Chem.*, 1913, **83**, 171 ; *A.*, i, 435.
[86] *Ber.*, 1912, **45**, 3431 ; *A.*, i, 150.
[87] C. Mannich, *Annalen*, 1912, **394**, 223 ; *A.*, i, 87.

corresponding amino-compound.[88] In addition to the above, a large number of other new glucosides have been described, in the course of the past year, which have also been prepared through the agency of acetobromoglucose. Mention should be made of a series of terpene glucosides,[89] as work of this nature is of obvious importance in view of the possibility that certain terpenes and sugars may have a common origin. In this connexion, it is perhaps not unimportant that terpenes and reducing sugars are occasionally encountered in the degradation products of naturally occurring substances.[90]

Another important series of syntheses, also carried out by means of acetobromoglucose, has resulted in the formation of the glucosides of sitosterol, cholesterol, and other closely related hydroxy-compounds.[91] The sitosterolglucoside was found to possess properties closely resembling the phytosterolines, and although the other glucosides described have not yet been detected among natural products, their characterisation may well prove useful in facilitating further research on the occurrence of carbohydrate complexes in plants.

As usual, a considerable number of publications have dealt with the subject of photosynthesis, and the majority of the researches under this heading have been directed towards duplicating the reactions involved in the natural formation of plant products. Generally speaking, it may be said that much of the recent work on the distribution of formaldehyde in plants, and the transformations undergone by the compound under the action of light, supports the idea that the aldehyde is the original source of the sugars, but that the condensation requires light energy.

An astonishing result is reported by Stoklasa, who, along with his collaborators, has been engaged for several years in studying the influence of ultra-violet rays in promoting the reduction of carbonic acid.[92] In a prolonged experiment, carried out with a generous supply of material at the radium factory at Joachimsthal, the effect of radium emanation in influencing this change has been ascertained. He finds that hydrogen and carbon dioxide react in the presence of potassium hydrogen carbonate to give formaldehyde, which polymerises to a mixture of reducing sugars. The latter were converted into the phenylosazones, which, on crystallisation,

[88] *T.*, 1913, **103**, 41.

[89] J. Hämäläinen, *Biochem. Zeitsch.*, 1913, **49**, 398 ; **50**, 209 ; *A.*, i, 497, 639.

[90] E. Sieburg, *Arch. Pharm.*, 1913, **251**, 154 ; *A.*, i, 639.

[91] A. H. Salway, *T.*, 1913, **103**, 1022.

[92] J. Stoklasa, J. Šebor, and W. Zdobnický, *Compt. rend.*, 1913, **156**, 646 ; *A.*, i, 342.

were separated into two distinct fractions. So far, the results are consistent with those of other researches, but the important claim is made that the sugars formed are optically active and give $[\alpha]_D$ +17·58°. Scrutiny of the experimental details reveals the fact that this statement is based on a very small polarimetric reading determined on a solution containing about 1 per cent. of (presumably) active material, and, in the meantime, most chemists will share the hesitation, expressed in a footnote to the original paper, with which Maquenne received this highly abnormal result.

Glucosamine.—The chemistry of glucosamine continues to attract attention, and a considerable amount of progress has been made. In last year's Report, the conversion of the amino-sugar into *d*-glucose was described, and recently a brief account of a second method of removing the amino-group has been given.[93] Methylglucosamine, when condensed with benzaldehyde in presence of hydrogen chloride, was converted into benzylidenemethylglucosamine hydrochloride. This compound, when acted on with an alkaline solution of sodium nitrite, was converted into a benzylidenehexose, and the final step in the series of reactions was the removal of the benzylidene group by the action of dilute acid. Contrary to expectation, the hexose formed was *d*-mannose. As glucosamine may thus be converted into either *d*-glucose or *d*-mannose, a change of the nature of a Walden inversion must take place in one of the processes. In the meantime, it would appear that there is no necessity to modify the views previously expressed, in which glucosamine is regarded as a derivative of glucose.

Among new derivatives of glucosamine, a series of important compounds has recently been synthesised by Weizmann and Hopwood,[94] who have succeeded in preparing complexes containing glucosamine and aminoacyl residues. The method followed was to condense glucosamine hydrochloride with α-bromoacyl haloids in the presence of alkali, and to act on the products with cold aqueous ammonia. The ultimate compounds obtained were anhydrides of α-aminoacylglucosamines, and the development of the research will be awaited with much interest.

The formation of a series of glucosides derived from glucosamine has also been described in the course of the year.[95] By condensing bromotriacetylglucosamine with hydroxy-compounds, in the presence of a base such as morphine, a series of acetylated aminoglucosides were obtained, from which the acyl groups were removed by cautious

[93] J. C. Irvine and A. Hynd, *P.*, 1913, **29**, 306.
[94] *Proc. Roy. Soc.*, 1913, A, **88**, 455; *A.*, i, 958.
[95] J. C. Irvine and A. Hynd, *T.*, 1913, **103**, 41.

hydrolysis. Amino-glucosides differ greatly in their behaviour towards hydrochloric acid, in some cases hydrolysis proceeding normally, and in others only with the utmost difficulty. For this reason it is suggested that the two types are differently constituted, the stable forms being *N*-cyclic compounds, whilst the others are regarded as normal glucosides. α-Aminohelicin and α-aminosalicin are among the representatives of the latter class, and compounds of this type may possibly occur in nature.

In this connexion it may be noted that a new glucosamine derivative, termed *lycoperdin*, has been isolated from the fungus, *Lycoperdum gemmatum*. This compound, to which the formula $C_{13}H_{24}O_9N_2$ has been ascribed, exists in two modifications, and although the linking of the two glucosamine residues present in the molecule has not been determined with certainty, the substance possesses a special interest in view of its comparative simplicity.[96] Incidentally it may be pointed out that the occurrence of glucosamine among plant products does not of necessity involve the pre-existence of glucoproteins, and an instructive paper by Viehoever[97] shows that chitin may be the original source of the amino-sugar. At the same time the claim made in this paper that bacteria, like certain fungi, contain chitin cannot be regarded as finally established in view of the results of other workers.[98]

Tannin.

On the publication last year of two papers by Fischer and Freudenberg, it was evident that the chemistry of tannin had entered on a new phase.[99] The idea then put forward that tannin may be regarded as essentially a pentadigalloylglucose has been supported in a number of indirect ways during the current year, and has stimulated the synthesis of complex derivatives of glucose possessing high molecular weights. The tannin problem, although far from being solved, may at least now be regarded as one which can reasonably be discussed under the general heading of carbohydrate derivatives, and for some time to come, work in this field is likely to be extended by the synthetical methods usually employed in the sugar group.

If tannin is to be regarded as a substituted glucose, the optical activity of the complex becomes an important factor, and recent work[1] has gone to show that in determinations of the specific

[96] Y. Kotake and Y. Sera, *Zeitsch. physiol. Chem.*, 1913, **88**, 56; *A.*, i, 1212.
[97] *Ber. Deut. bot. Ges.*, 1912, **30**, 443; *A.*, i, 142.
[98] T. Koźniewski, *Bull. Acad. Sci. Cracow*, 1913, **10**, A, 942; *A.*, i, 428.
[99] *Ber.*, 1912, **45**, 915, 2709; *A.*, 1912, i, 471, 887.
[1] E. Navassart, *Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 97; *A.*, i, 383.

rotation of tannin the effect of the solvent and of variations in the concentration are very great. The maximum activity is shown in aqueous solution, and the value increases greatly with dilution, ultimately reaching $[\alpha]$ 89·7° for $c=0{\cdot}08$. In alcohol, on the other hand, the specific rotation is much lower, and the variation with change of concentration is small. It is, of course, extremely doubtful if much trust can be placed in determinations of the rotatory power of tannin in concentrated solution, but the figures quoted by Navassart for low concentrations show a general resemblance to those previously determined by Fischer. On the other hand, the values disagree with those recorded for tannin isolated from Turkish galls.

The observation[2] that glucogallic acid occurs associated with tannin is of evident importance, and the properties of the compound have now been further described. The acid is optically active, and although it reduces Fehling's solution it apparently possesses the glucosidic structure, and is hydrolysed to give glucose and gallic acid. As the compound is a comparatively simple substance compared with tannin, the evidence of hydrolysis may be regarded as direct and convincing, pointing to the fact that glucose, in combination with gallic acid, is naturally associated with tannin. Unfortunately, it has proved impossible to verify the nature of Feist's glucogallic acid by synthesis. Through the agency of acetobromoglucose, Fischer and Strauss[3] have prepared a β-glucosidogallic acid, which has the normal structure:

$$C_6H_{11}O_5{\cdot}O{\cdot}C_6H_2(OH)_2{\cdot}CO_2H.$$

Although the compound shows many similarities with the "glucogalline" described by Gilson,[4] it is certainly different from Feist's product. This difference cannot be explained on the assumption that the latter is the α-modification of the glucoside, and the two compounds are probably fundamentally distinct, judging from their behaviour on hydrolysis.

A definite step towards the synthesis of a penta-*m*-digalloylglucose has been made through the discovery of an improved method for preparing *m*-digallic acid in quantity.[5] The structure of the compound has been confirmed by methylation, and it would appear that it is identical with the digallic acid previously described as the para-compound. The synthesis of a pentadigalloylglucose has so far not been carried out, but in view of the successful preparation of the glucose derivatives containing

[2] K. Feist, *Arch. Pharm.*, 1912, **250**, 668; *A.*, i, 70.
[3] *Ber.*, 1912, **45**, 3773; *A.*, i, 180.
[4] E. Gilson, *Compt. rend.*, 1903, **136**, 386; *A.*, 1903, i, 355.
[5] E. Fischer and K. Freudenberg, *Ber.*, 1913, **46**, 1116; *A.*, i, 479.

aromatic substituents of high molecular weight, which are described in the paper referred to, there is every reason to hope that the synthesis of the essential constituent of tannin will not be long delayed. Attention should also be drawn to a summary of the present position of the chemistry of tannin which has been given by Fischer in the form of an address.[6] This development must have the effect of directing attention to the fact that the sugar molecule can function as a nucleus in the formation of huge molecular complexes, in that there seems no practical limit to the magnitude of the substituents which may replace the hydroxyl groups. Possibly also, in future work on the cleavage of natural compounds, there will be less tendency to disregard, as insignificant and unimportant, the small proportions of reducing sugars which are frequently formed in such reactions.

Enzyme Synthesis.

Any review dealing with the action of enzymes may readily overlap with other sections of the Annual Reports, and consequently references which may be suitably included under the chemistry of aliphatic compounds must of necessity be brief, and can give only a slender idea of the volume and importance of the work now being carried out in this field. Generally speaking, the present tendency of researches on enzyme action is to concentrate on two types of problem, namely, (1) synthetic reactions promoted by enzymes, and (2) the mechanism of fermentations. Regarding the latter question, the original literature up to 1910 has been included by Harden in his monograph on alcoholic fermentation, and it thus appears desirable, in the meantime, to limit the present review to noting the recent advances in enzyme synthesis.

A useful summary of the work which has been carried out during the past three years on the synthesis of glucosides by means of emulsin has been recently compiled by Bourquelot and Bridel,[7] but it invites the criticism that a growing tendency exists to publish results in small, fragmentary sections, and in an incomplete state. The general principle underlying enzyme synthesis is that the equilibrium between a sugar and a glucoside, when in contact with the appropriate enzyme, can be displaced in the direction of the glucoside when the solvent contains excess of the hydroxy-component of the glucoside. Most of the recent work has thus dealt with the action of enzymes on sugars dissolved in alcohols containing varying amounts of water, or in some cases acetone.

[6] E. Fischer, *Ber.*, 1913, **46**, 3253; *A.*, i, 1352.
Ann. Chim. Phys., 1913, [viii], **28**, 145; *A.*, i, 781.

When emulsin is employed, the β-form of the hexoside is produced,[8] and the following may be mentioned as typical examples of β-compounds synthesised in this way: methylglucoside, benzylgalactoside, geranylglucoside, and cinnamylglucoside. The disaccharide gentiobiose has also been synthesised in a similar manner from glucose.[9] The compounds can apparently be isolated in a remarkably pure condition, and in some cases have been obtained crystalline when ordinary synthetic methods give rise merely to amorphous products. Considerable attention has been given to proving that the same enzyme carries out both hydrolytic and synthetic actions. Thus, solutions of dextrose in dilute methyl alcohol, and of β-methylglucoside in the same solvent, undergo oppositely directed actions under the influence of emulsin, the rates of hydrolysis and synthesis are the same, and the same equilibrium is reached from both directions.[10] A similar conclusion is arrived at in the case of β-ethylglucoside, and Bayliss, in a study of the system glycerol, dextrose, glycerolglucoside and water, has obtained the same result.[11]

It is evident that the possibilities of enzyme synthesis are almost unlimited, and must have an important bearing in the future on the chemistry of the natural fats and carbohydrates, but considerable caution must still be exercised in drawing conclusions from the results, owing to the difficulty in obtaining individual enzymes or even standardised mixtures of enzymes. This applies with special force to emulsin, which has been shown by H. E. Armstrong and others[12] to contain several closely-related enzymes, and an instructive case which emphasises this point is quoted by Krieble, who found that an emulsin which synthesised *l*-mandelonitrile produced the *d*-isomeride two years later.[13]

In addition to emulsin, the enzyme contained in the aqueous extract of bottom yeast has also been used in the synthesis of glucosides, but in this case the α-forms are produced. As a necessary part of this line of investigation, a considerable amount of work has been done during the past year on the proportions of

[8] E. Bourquelot and H. Hérissey, *Compt. rend.*, 1912, **155**, 1552; *A.*, i, 213; J. Hämäläinen, *Biochem. Zeitsch.*, 1913, **52**, 409; *A.*, i, 888; E. Bourquelot and M. Bridel, *Compt. rend.*, 1913, **157**, 72; *A.*, i, 888; *J. Pharm. Chim.*, 1913, [vii], **8**, 15; *A.*, i, 1007.

[9] E. Bourquelot, H. Hérissey and J. Coirre, *Compt. rend.*, 1913, **157**, 732; *A.*, i, 1305.

[10] E. Bourquelot and M. Bridel, *loc. cit.*; E. Bourquelot and E. Verdon, *Compt. rend.*, 1913, **156**, 957; *A.*, i, 542.

[11] W. M. Bayliss, *J. Physiol.*, 1913, **46**, 236; *A.*, i, 919.

[12] *Proc. Roy. Soc.*, 1912, B, **85**, 359; *A.*, 1912, i, 816.

[13] *Biochem. Bull.*, 1913, **2**, 227; *A.*, i, 663, 1255.

various alcohols which may be employed in enzyme actions without destroying the activity of the catalyst, and in ascertaining the temperature limits of these reactions.[14]

It would be unfortunate if the success which has attended researches on enzyme synthesis had the effect of distracting attention from the problems involved in the hydrolytic actions of enzymes. The two types of inquiry are naturally intimately connected, and the time seems to have come when the synthetical researches should be directed, not so much to the multiplication of new examples, as to systematic attempts to interpret the changes involved. A paper by Prof. and Dr. Armstrong,[15] which contains a critical discussion of their experimental work on the nature of enzyme action, with particular reference to hydrolysis, has an important bearing on the question of enzyme synthesis. Owing to the closely-sustained reasoning involved, it is impossible to refer to the details of this important paper, but the original should be consulted by all who are attracted to the subject of enzyme action generally.

Cellulose.

It is only natural that a large proportion of the current researches on cellulose should have a direct technical bearing, and it is a difficult matter to select, from the mass of somewhat empirical work, such investigations as are likely to lead to theoretical developments. It can, however, still be said that the difficulties of the problem do not prevent numerous workers from endeavouring to gain some insight into the structure of the cellulose complex, and an important step has been made as the result of independent researches by Ost,[16] and by Willstätter and Zechmeister.[17] The latter observers have traced, polarimetrically and gravimetrically, the hydrolysis of cellulose when dissolved in concentrated hydrochloric acid. Their results lead to the conclusion that the dextrose formed amounts to 96 per cent. of the value calculated on the assumption that cellulose is wholly composed of dextrose residues. In a subsequent paper,[18] Ost criticises the validity of Willstätter's method, and claims, with some justice, that the older process, in which cellulose is first dissolved in sulphuric acid and the hydrolysis completed in a highly diluted solution, is less open

[14] E. Bourquelot and M. Bridel, *J. Pharm. Chim.*, 1913, [vii], **7**, 27 ; *A.*, i, 212, 303, 428 ; F. Keeble, E. F. Armstrong, and W. N. Jones, *Proc. Roy. Soc.*, 1913, B, **86**, 308 ; *A.*, i, 803.

[15] H. E. Armstrong and E. F. Armstrong, *Proc. Roy. Soc.*, 1913, B, **86**, 561 ; *A.*, i, 1116.

[16] H. Ost and L. Wilkening, *Chem. Zeit.*, 1910, **34**, 461 ; *A.*, 1910, i, 364.

[17] *Ber.*, 1913, **46**, 2401 ; *A.*, i, 955.

[18] *Ibid.*, 2995 ; *A.*, i, 1148.

to objection. The results arrived at by both workers are, however, practically identical so far as the dextrose content of cellulose is concerned. Further confirmation of this important point has been gained by Ost in his study of the hydrolysis and acetolysis of cellulose, in that he finds the combined yield of dextrose and cellobiose acetates agrees with the supposition that only dextrose residues are present in cellulose.[19]

The linking of the dextrose groups in cellulose is a problem which has aroused considerable discussion in the past, but direct experimental evidence bearing on the question is difficult to obtain. A recent paper[20] indicates, however, a new line of attack. The method proposed is to methylate cellulose completely, and to subject the product to acid hydrolysis. A mixture of methylated dextroses should thus be produced, and the determination of the number and distribution of the alkyl groups in each sugar would then give a direct clue to the union of the monosaccharide residues in the parent complex. The research has meanwhile not proceeded far enough to show if the hopes of the workers will be fully realised, but the results are interesting. The alkylation, which was effected by means of methyl sulphate, shows a distinct tendency to be arrested at the definite stages indicated in the formulæ $C_{12}H_{19}O_9 \cdot OMe$ and $C_6H_9O_4 \cdot OMe$.

It is perhaps significant that in the latter compound the cellulose derivative still retains the capacity to form a xanthate, and that the methyl group survives the reaction, and is present in the "regenerated cellulose."

Despite numerous and laborious investigations, the nature of the derivatives of cellulose termed "hydrocelluloses" and "oxycelluloses" still remains vague and uncertain. It may be noticed[21] that Ost has abandoned his previous view that cellulose and hydrocellulose differ in composition, and he now regards the latter as merely possessing a smaller molecular magnitude. His conclusions have, however, already been questioned. Similarly, the opinion has again been put forward[22] that α-oxycellulose differs from cellulose, not in composition, but only in the nature of the fibrous structure, and that β-oxycellulose consists merely of degradation products. This state of confusion is perhaps not to be regretted, as attention must necessarily be directed to ascertaining the rôle of surface conditions in affecting reactions carried out on organised structures.

[19] *Annalen*, 1913, **398**, 313; *A.*, i, 833.
[20] W. S. Denham and Miss H. Woodhouse, *T.*, 1913, **103**, 1735.
[21] *Loc. cit.*
[22] C. Piest, *Zeitsch. angew. Chem.*, 1913, **26**, 24; *A.*, i, 250.

It is a noteworthy fact that, outside of biochemical investigations, very few publications have recently dealt with the chemistry of starch or inulin. Further information as to the molecular complexity of starch has been gained by subjecting potato starch to the action of enzymes, and precipitating the degradation products at definite intervals.[23] The approximate mean molecular weight, when determined by viscosity measurements, showed regular variations in magnitude. In amylodextrins the value was above 10,000, decreasing in erythrodextrins to 6200—7000, and, ultimately, in achroodextrins to about 3700. Finally, it has been shown,[24] by direct measurement of osmotic pressures, that the molecular magnitude of dextrin-β is approximately 950 ± 50. It will be seen that this value, which agrees well with those obtained by other processes, corresponds with a hexa-amylose. The simpler amyloses are substances of considerable interest, and a detailed account of their properties is contributed by Pringsheim and Eissler in a recent paper.[25]

Nitrogen Compounds: Theories of Structure.

In view of the fact that during the past two years several important papers have appeared dealing with the theoretical questions presented by nitrogen compounds, it has been considered advisable to place severe limitations on the number of references to investigations which are mainly of a descriptive or purely experimental nature.

A problem of long standing, the distribution of the nitrogen valencies, has once more been brought within the range of discussion as the result of the isolation of amino-oxides of the type $a:Nbcd$ in optically active modifications.[26] The assumption made by Meisenheimer that the five valencies are not inter-equivalent has now been subjected by him to experiment, and, selecting trimethylamine oxide as a test substance, he has carried out the reactions indicated below[27]:

$$Me_3N{:}O \xrightarrow{RI} Me_3N\begin{matrix}OR\\I\end{matrix} \xrightarrow{NaOH} Me_3N\begin{matrix}OR\\OH\end{matrix}$$

$$Me_3N{:}O \xrightarrow{HCl} Me_3N\begin{matrix}OH\\Cl\end{matrix} \xrightarrow{NaOR} Me_3N\begin{matrix}OH\\OR\end{matrix}.$$

It should be noted that the final products were not isolated in the pure condition, but their reactions in solution indicate that the substances are isomeric and not identical. Further, the isomerism

[23] W. Biltz, *Ber.*, 1913, **46**, 1532; *A.*, i, 707.
[24] W. Biltz and W. Truthe, *ibid.*, 1377; *A.*, i, 593.
[25] *Ber.*, 1913, **46**, 2959; *A.*, i, 1156.
[26] J. Meisenheimer, *Annalen*, 1911, **385**, 117; *A.*, 1912, i, 25.
[27] *Ibid.*, 1913, **397**, 273; *A.*, i, 595.

has been shown to extend to compounds of the type $Me_3N<^{OR}_{OR'}$ and $Me_3N<^{OR'}_{OR}$, where again the decomposition reactions lead to the conclusion that the alkyloxy-groups are attached to the nitrogen atom in a different manner. Other structural representations may, however, account for the isomerism. For example, the formulæ $Me_3N{:}O<^{OR}_{R'}$ and $Me_3N{:}O<^{OR'}_{R}$, which are based on the oxonium type, would explain the existence of two forms, but these and other alternatives are rejected by Meisenheimer. He ultimately comes to the conclusion that in ammonium compounds nitrogen is definitely quinquevalent, and the units attached to four of the principal valencies occupy an inner zone, exterior to which is the atom or group attached to the fifth principal valency. Further, he imagines the outer group to have no fixed position, and, in consequence, to have no influence on the asymmetry. According to this view, the isomerides mentioned above could be represented by such formulæ as $[Me_3N{\cdot}OR]{\cdot}OR'$ and $[Me_3N{\cdot}OR']{\cdot}OR$, and the suggestion is made that similar considerations may even be applied to phosphonium compounds.

These ideas have not been allowed to remain long unchallenged.[28] It has been pointed out that if isomeric compounds of the type $Me_3N(OR)OH$ do exist, they may be regarded as alcoholates of a feeble base, $Me_3N(OH)_2$, and, as such, would be hydrolytically dissociated by water to give identical products. In order to account for the existence of the second isomeride, Fromm is disposed to regard the action of methyl iodide on trimethylamine oxide as resulting in the formation of an oxonium methiodide, which, on treatment with alkali, would be converted into $Me_3N{:}O<^{Me}_{OH}$.

The present position of the resulting argument is that, whilst the authors concerned agree that in ammonium compounds there are four negative valencies and one positive valency, Fromm is unwilling to admit that these considerations apply equally to amino-oxides, which he regards as exercising negative and positive valencies in the proportion 3 : 2. Another ratio, that between speculation and experiment, will be an important factor in determining the progress likely to be made in this discussion.

A result which has a direct bearing on the nature of the nitrogen valencies was obtained in the course of a research on the resolution of phenylmethylethylazonium iodide,[29] as, during the preparation

[28] E. Fromm, *Annalen*, 1913, **399**, 366 ; *A.*, i, 1047.

[29] B. K. Singh, *T.*, 1913, **103**, 604.

of the compound, it was found that the order in which the alkyl groups are introduced does not affect the constitution of the resulting product. This result is opposed to the idea originally advocated by LeBel, but is not inconsistent with Meisenheimer's later views.

Current ideas regarding the structure of aliphatic diazo-compounds have no doubt been greatly influenced by Thiele's adherence to the view that diazomethane and hydrazoic acid may be represented by the formulæ $CH_2{:}N{:}N$ and $HN{:}N{:}N$ respectively. Fresh experimental evidence on this question is now available,[30] as it has been shown that the action of Grignard reagents on diazocamphor and diazodeoxybenzoin proceeds, in conformity with Thiele's views, to give the substituted hydrazone corresponding with the parent diketone:

$$C_8H_{14}\begin{cases}CN_2\\CO\end{cases} \xrightarrow{MgPhBr} C_8H_{14}\begin{cases}C{:}N{\cdot}NH{\cdot}C_6H_5\\CO\end{cases}.$$

$$\begin{matrix}C_6H_5{\cdot}CN_2\\C_6H_5{\cdot}CO\end{matrix} \xrightarrow{MgMeI} \begin{matrix}C_6H_5{\cdot}C{:}N{\cdot}NH{\cdot}CH_3\\C_6H_5{\cdot}CO\end{matrix}.$$

On the other hand, the products to be expected if the nitrogen atoms are linked in a cyclic structure would be respectively:

$$C_8H_{14}\begin{cases}CH{\cdot}N{:}N{\cdot}C_6H_5\\CO\end{cases} \quad \text{and} \quad \begin{matrix}C_6H_5{\cdot}CH{\cdot}N{:}N{\cdot}CH_3,\\C_6H_5{\cdot}CO\end{matrix}$$

and the possibility still remains that azo-compounds of this type would escape detection in view of their ready transformation into the isomeric substituted hydrazones. Unfortunately, the reaction between diazodeoxybenzoin and magnesium phenyl bromide, which might be expected to settle this point, followed an unexpectedly complex course. The results obtained in the investigation now referred to are certainly direct and emphatic. In the original paper it is, however, pointed out that many reactions of aliphatic diazo-compounds which may be claimed to support Thiele's views are equally well explained in terms of the older cyclic formulæ. Thus, the preparation of diazomethane from hydrazine was regarded by Staudinger and Kupfer[31] as involving the changes $H_2N{\cdot}NH_2 \longrightarrow >C{:}N{\cdot}NH_2 \longrightarrow H_2C{:}N{:}N$. It is, however, possible that the part played by chloroform in this reaction consists in condensation with an amino-group, followed by the elimination of a third molecule of hydrogen chloride:

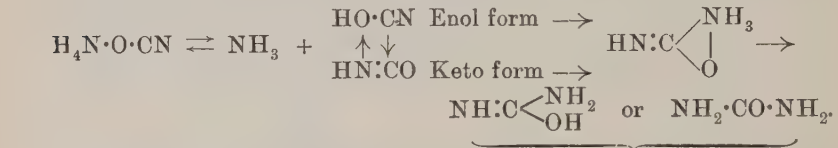
$$\begin{matrix}H\\Cl\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}Cl\\Cl\end{matrix} + H_2N{\cdot}NH_2 \longrightarrow \begin{matrix}H\\Cl\end{matrix}\!\!>\!C{:}N{\cdot}NH_2 \longrightarrow$$

$$HC\begin{cases}N\\NH\end{cases} \longrightarrow H_2C\begin{cases}N\\\|\\N\end{cases}.$$

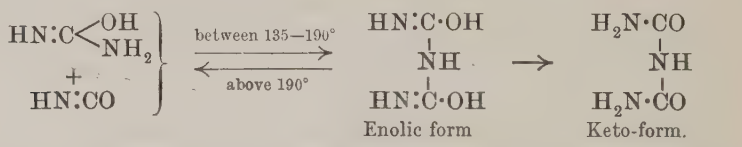
[30] M. O. Forster and D. Cardwell, *T.*, 1913, **103**, 861.

[31] H. Staudinger and O. Kupfer, *Ber.*, 1912, **45**, 501 ; *A.*, 1912, i, 245.

Any review of theoretical developments in the chemistry of nitrogen compounds would be incomplete without reference to views recently expressed as to the mechanism of the formation of carbamide from ammonium cyanate.[32] In last year's Report an account was given of Chattaway's theory of the change, and this has now been criticised by Werner, who offers an alternative explanation. It is maintained that the fundamental factors governing the reaction are (*a*) dissociation of the ammonium salt, and (*b*) the establishment of equilibrium between the isomeric forms of cyanic acid as expressed by the scheme:



A number of arguments and experimental results are quoted in support of the above view, and, more recently,[33] a quantitative study of the formation of biuret has strengthened the argument materially. It has been shown that the formation and decomposition of biuret may be regarded as a reversible reaction between carbamide and the "keto-form" of cyanic acid:



In the meantime it would be premature to weigh the claims of the rival theories, and a critical comparison of their merits may thus be reserved.

Amino-compounds.

Although a large number of investigations have lately been concerned with amino-compounds, the main result has been the simplification and extension of working methods rather than the development of any novel theoretical problems. As examples of new or improved practical processes likely to find useful application, reference may be made to the fact that the method of preparing secondary amines from acids has now been applied with highly satisfactory results to the production of disecondary amines from dicarboxylic acids,[34] and, in another useful paper, directions are given whereby the yields of alkylamines obtained from nitriles may be greatly improved by simple modifications of Ladenburg's

[32] E. A. Werner, *T.*, 1913, **103**, 1010.
[33] *Ibid.*, 2275. [34] H. R. Le Sueur, *ibid.*, 1119.

method.[35] Workers who have occasion to study acid amides will also welcome the observation that Hofmann's method of preparing these compounds can be adjusted to give good results,[36] and may find it necessary to consult a paper on the application of Hofmann's reaction to dialkylacetamides.[37]

A suggestive paper by Meisenheimer offers a novel explanation to account for the formation of dialkylchloroamines by the action of hypochlorous acid on tertiary amines.[38] The idea is put forward that in the first stage of this reaction a trialkylamine dichloride is formed, and this in turn gives rise to an unsaturated derivative:

$$N(CH_3)_3 \longrightarrow N(CH_3)_3Cl_2 \longrightarrow N(CH_3)_2(:CH_2)Cl.$$

In the above example, the final reactions consist in the formation of formaldehyde and dimethylamine hydrochloride, which is then decomposed by the excess of hypochlorous acid. The theory certainly seems to be in good agreement with the experimental results, but it is very doubtful if it is consistent with the properties of trialkylamine dihaloids, so far as these are known from the study of trimethylamine dibromide.

Amino-acids.—Attempts have frequently been made to isolate definite condensation products from the action of formaldehyde on amino-acids, but, as a rule, the methods employed have been somewhat drastic, and although the products show many similarities with the polypeptides, their formation doubtless involves profound molecular changes. In recent work, which has led to more definite results, it has been shown that under carefully regulated conditions, the action of formaldehyde on glycine is to give a stable methylenediglycine, $CH_2(NH{\cdot}CH_2{\cdot}CO_2H)_2$, and, further, that in the presence of reducing agents the reaction gives rise to sarcosine and dimethylaminoacetic acid.[39] This method of methylating amino-acids possesses many practical advantages, and will doubtless find considerable application.

A synthetic method of building up complexes containing amino-acyl residues depends on the fact that ethyl chloroglyoxalate may be condensed with esters of amino-acids in the form of their salts. The product can then be coupled with a different amino-acyl group by condensation with the potassium salt of a second amino-acid. For example, ethyl chloroglyoxalate and methyl α-aminopropionate hydrochloride give, according to the first-mentioned reaction, methyl ethyloxalyl-α-aminopropionate, $CO_2Et{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2Me$, and

[35] J. N. Rakshit, *J. Amer. Chem. Soc.*, 1913, **35**, 444; *A.*, i, 606.
[36] H. Decker, *Annalen*, 1913, **395**, 282; *A.*, i, 272.
[37] F. L. Pyman, *T.*, 1913, **103**, 852.
[38] *Ber.*, 1913, **46**, 1148; *A.*, i, 447.
[39] W. Löb, *Biochem. Zeitsch.*, 1913, **51**, 116; *A.*, i, 709.

subsequent reaction with potassium aminoacetate gives methyl glycineoxalyl-α-aminopropionate,

$$CO_2H\cdot CH_2\cdot NH\cdot CO\cdot CO\cdot NH\cdot CHMe\cdot CO_2Me,$$

which serves as a type of a large number of compounds synthesised by this method.[40]

It is quite evident that the investigation of complex amino-acids is in the meantime being prosecuted by biochemical rather than by synthetical methods, and this state of affairs will no doubt continue until further study of the Walden inversion has removed the restrictions and uncertainties at present attending the synthesis of optically active compounds.

JAMES COLQUHOUN IRVINE.

PART II.—HOMOCYCLIC DIVISION.

The mass of literature which comes under review for the purposes of this section of the Annual Reports has shown no falling off, but rather an increase this year; the number of papers which had to be considered amounted nearly to 400. Within the limits which are imposed, it is impossible to deal with the great majority of these researches. In this particular region of the subject any intelligible account of much of this work demands no inconsiderable space. The writer is very conscious of the fact that he has omitted much of importance in making his selection. Many of the researches are mainly extensions in detail; an unusual number of "new" compounds have been described. Others of more general interest are obviously of the nature of interim reports, and can in consequence be more appropriately considered at a later time. The survey of the results of this huge chemical activity has impressed the present writer with the truth of the statement made by a former President of the Society, that the great obstacle to advancement lies in the lack of co-ordination of this new knowledge; to "integrate" this information is the pressing task.

The Structure of Benzene and Naphthalene.

After the vigorous discussions on the structure of the benzene nucleus, started partly by the discovery of *cyclo*octatetraene, which was a feature of 1912, this year's literature contains but an aftermath. This renewed examination of the problem left the "centric" formula, of all the hypotheses, as the most suitable symbol for representing the unique character of benzene. During

[40] D. J. Meyeringh, *Rec. trav. chim.*, 1913, **32**, 140; *A.*, i, 834.

the period under review the exact meaning of the singular absence of free affinity in benzene, and hence the question of the representation of the disposal of the residual affinity, have formed the subject of a gentle exchange of opinion.[1]

Much labour has been expended on a study of the absorption spectra of benzene and its simpler substituted derivatives. The absorption of the vapour has been examined rather than that of the solutions, as generally, owing to the absence of the damping effect of the solvent, the detection of the delicacies of the selective absorption becomes possible; and, further, there is no confusion, owing to absorption by the medium, especially in the more refrangible region.[2]

A very careful comparative study of the ultraviolet absorption of benzene (as vapour) and of *cyclo*hexene and $\Delta^{1:3}$-*cyclo*hexadiene has emphasised the peculiar relations of the six carbon atoms of the benzene nucleus.[3] By means of a fluorspar spectrograph Stark obtained photographic records in regions beyond those reached by previous investigators, in fact, as far as $\lambda = 185 - 180\ \mu\mu$, and has thus found indications of extreme ultraviolet absorption bands, even in saturated hydrocarbons, such as *cyclo*hexane and camphane, as well as in unsaturated compounds. *cyclo*Hexene and *cyclo*hexadiene show the two unresolved broad bands in the ultraviolet region, in both cases similar to those characteristic of the ethylene linking. The conjugation of the linkings in the latter causes a shifting of the bands towards the visible spectrum, and at the same time an intensification of the less refrangible band. Benzene gives a totally different spectrum from either of these hydrocarbons; besides the known group of narrow bands, $\lambda = 270 - 230\ \mu\mu$,[4] there is an intense group of similar narrow bands at $\lambda = 210 - 190\ \mu\mu$. It is urged, therefore, that in benzene a specific relation exists between the carbon atoms, which is quite distinct from the ordinary ethylene (or acetylene) linkings. The term "benzene-linking" is suggested—a relation perhaps best represented in our usual symbols by the Armstrong centric formula.

[1] K. Gebhard, *J. pr. Chem.*, 1912, [ii], **86**, 540; 1913, [ii], **88**, 94; *A.*, i, 28, 841. H. von Liebig, *ibid.*, 1913, [ii], **87**, 393; *A.*, i, 607. Compare also W. P. Wynne, Presidential Address to the Chemical Section of the British Association, 1913.

[2] J. E Purvis and N. P. McCleland, *T.*, 1913, **103**, 1088. J. E. Purvis, *ibid.*, 1638. J. J. Fox and F. G. Pope, *ibid.*, 1263. H. S. Fry, *Zeitsch. physikal. Chem.*, 1913, **82**, 665; *A.*, ii, 363. N. A. Valiaschko, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 199; *A.*, ii, 367. G. Weimer, *Zeitsch. wiss. Photochem.*, 1913, **12**, 33; *A.*, ii, 367.

[3] J. Stark and P. Levy, *Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 139, 175, 179; *A.*, ii, 363, 365, 366.

[4] W. N. Hartley, *T.*, 1881, **39**, 153; 1885, **47**, 685; 1887, **51**, 152; *Phil. Trans.*, 1907, **A, 208**, 475; *A.*, 1908, ii, 243.

The most recent consideration of the molecular refraction of benzene,[5] on the other hand, appears to indicate conclusively that there are three ethylene linkings in the molecule of benzene. It may be argued, however, that the agreement between the calculated and found values of the molecular refraction is purely accidental; the unique "benzene-linking" may possess a refractivity which produces the same divergence as three normal (conjugated) ethylene linkings.

The complete change in the spectra (vapour), which is brought about by the substitution of hydrogen by a hydroxyl or an amino-group,[6] is a difficulty in the way of such a rigid association as Stark suggests, between the spectrum, more especially in the case of benzene, and a particular type of carbon-linking.

Naphthalene.—The unexpected properties of *cyclo*octatetraene led Willstätter and Waser [7] to decide in favour of Harries' centric-ethylene formula for naphthalene in place of Bamberger's symmetric di-centric formula,[8] which, it should be noted, does not

contain a benzene nucleus. This symbol was, however, put forward with the reservation that no formula of the usual type completely represented the whole chemistry of naphthalene.[9] The high contrast between naphthalene and dihydronaphthalene on hydrogenation has led to a reversal of this opinion; Willstätter now leans to the di-centric formula.[10] The grounds are that Δ^1- and Δ^2-dihydronaphthalene yield tetrahydronaphthalene on reduction, in this behaviour resembling aromatic olefines, such as styrene and so forth. Naphthalene, on the other hand, yields only perhydro- and no tetrahydro-naphthalene, and in consequence cannot possess any normal ethylene linking, as Harries' formula demands.

Recent measurements of the absorption spectrum of naphthalene vapour favour the di-centric formula [11]; the absorption spectrum shows two groups of narrow bands in the ultraviolet region, very similar to the bands given by benzene, but somewhat nearer the visible spectrum. If Stark's contention that the nature of the carbon valence is the main factor in absorption be granted, it must

[5] F. Eisenlohr, *Jahrb. Radioaktiv. Elektronik*, 1912, **9**, 315; *A.*, 1912, ii, 709.
[6] Purvis, *loc. cit.*; Fox and Pope, *loc. cit.*
[7] *Ber.*, 1911, **44**, 3423; *A.*, 1912, i, 27; *Ann. Report*, 1912, 113.
[8] *J. pr. Chem.*, 1890, [ii], **42**, 194; *A.*, 1890, 1304.
[9] E. Bamberger, *Ber.*, 1913, **46**, 1899; *A.*, i, 846.
[10] *Ber.*, 1913, **46**, 1051; *A.*, i, 455.
[11] J. Stark and P. Levy, *Jahrb. Radioaktiv. Elektronik*, 1913, **10**, 179; *A*, ii, 366. Compare W. N. Hartley, *T.*, 1885, **47**, 685.

be conceded that in naphthalene a linking closely resembling the benzene linking is present.

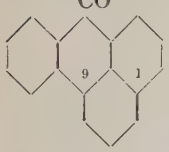
The strains or tensions in a series of six-membered conjugated or condensed ring systems are greater when the rings are in linear order than when the system is angular.[12] The tensions indicate that the system becomes labile in such a series of five rings. The theory was, failing simple carbon compounds, well illustrated by derivatives of the azine and acridine series, in which linear systems of five conjugated rings are found. The recent preparation of di- and tetra-hydrodinaphthanthracene,

$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4.$$

affords an interesting illustration of the theory[13] in rings composed solely of carbon atoms. Inasmuch as neither yields dinaphthanthracene on oxidation, but its decomposition products, it may be concluded that the linear hydrocarbon is highly unstable, and has, contrary to the statement in the literature, never been isolated.[14]

Friedel and Crafts' Reaction.

Notwithstanding the very extensive use of this reaction and the large number of most diverse applications to which aluminium chloride may be put, until recently little has been done to elucidate the manner in which this and similar catalysts act. Each year adds, not merely to the list of syntheses, but also to the types of reactions that can be brought about by its means. In the period under review an interesting development is worthy of mention, namely, the elimination of hydrogen, especially from aromatic nuclei, accompanied by the formation of more complex compounds with condensed nuclei.[15] The reaction takes place most easily in the case of ketones, when only a relatively low temperature (80—140°) is necessary. Thus 1:9-benzanthrone (annexed formula) is produced in excellent yield from phenyl α-naphthyl ketone. In a similar way a compound containing as many as ten condensed six-rings, 5:6:5′:6′-dibenzpyranthrone (formula on p. 98), has been prepared. 3:8-α-



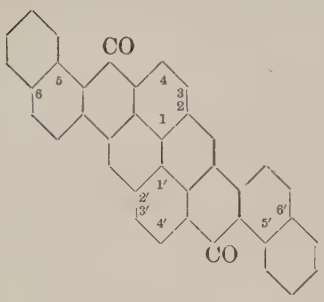
[12] O. Hinsberg, *Annalen*, 1901, **319**, 281; *A.*, 1902, i, 238; *Ber.*, 1903, **36**, 4051; *A.*, 1904, i, 200; *J. pr. Chem.*, 1913, [ii], **88**, 58; *A.*, i, 849.

[13] W. H. and Mrs. M. Mills, *T.*, 1912, **101**, 2194.

[14] F. Russig, *J. pr. Chem.*, 1900, [ii], **62**, 30; *A.*, 1900, i, 601.

[15] R. Scholl and C. Seer, *Annalen*, 1912, **394**, 111; *A.*, i, 56. Compare also R. Scholl and others, *Ber.*, 1907, **40**, 1691; 1910, **43**, 1734, 2202; *A.*, 1907, i, 540; 1910, i, 494, 616.

Naphthoylpyrene, which is itself obtained from pyrene and α-naphthoyl chloride in the presence of aluminium chloride, is converted into the pyranthrone on heating with the catalyst at 140°.



Aluminium chloride has been occasionally observed to behave abnormally, and to bring about simultaneously a side-reaction as well as the normal condensation.[16] Phthalic anhydride and *o*- and *p*-chlorotoluene give the corresponding chlorotolylbenzoic acids, but the two bromotoluenes yield one bromotolylbenzoic acid, which is probably the ortho-compound. Similar abnormalities have been found when the phthalic anhydride is replaced by benzoyl chloride; from the chlorotoluenes the expected condensed products are obtained, but the *m*- and *p*-bromotoluenes give mixtures owing to the migration of the halogen. In the case of *o*-bromotoluene the halogen is replaced by a hydroxyl group—a reaction not hitherto observed with aluminium chloride—and phenyl hydroxytolyl ketone is the sole product.

The Mechanism of Friedel and Crafts' Reaction.—It is a well-known fact that the quantity of aluminium chloride required to bring about condensations of acid chlorides and anhydrides with hydrocarbons varies very greatly with the constitution of the reacting substances. In some cases traces are sufficient, whilst in others a molecular proportion or more of the catalyst is necessary in order to obtain a good yield. This behaviour is not analogous to the ordinary effect of variation in the concentration of a catalyst, for it appears that a certain minimum quantity of the chloride must be present in the system in order that a reaction should follow. Similar observations have also been made with other metallic chlorides.

The isolation of additive compounds of aluminium chloride and acid chlorides, in the first instance by G. Perrier,[17] led to the general belief that the formation of such additive compounds was a necessary step in the Friedel and Crafts' and analogous reactions. The halogen compound (or the acid anhydride) is supposed to become active in this additive compound, and hence able to

[16] G. Heller and others, *Ber.*, 1908, **41**, 3627; *A.*, 1908, i, 994; *ibid.*, 1910, **43**, 2890; *A.*, 1910, i, 770; *ibid.*, 1912, **45**, 665, 792; *A.*, 1912, i, 357, 358; *ibid.*, 1913, **46**, 1497; *A.*, i, 631.

[17] *Compt. rend.*, 1896, **122**, 195; *A.*, 1896, i, 353; *Ber.*, 1900, **33**, 815; *A.*, 1900, i, 331. B. N. Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1310; *A.*, 1911, i, 45.

condense with the hydrocarbon. In recent years the knowledge of such co-ordinative compounds, in which the two units are attached by their residual affinity, has been greatly increased (Menschutkin, Pfeiffer and others); and the newer views on valency have given an easy means of representing them by the use of subsidiary linkings. The most diverse types of carbon compounds have been found to unite with many metallic chlorides, conspicuously those of iron, aluminium, tin, and antimony; the compounds even of benzene and other inactive hydrocarbons have been prepared.[18] There may be some evidence in a few cases that these co-ordinative compounds are more reactive than the simple organic substance, but generally it seems to be taken for granted, sometimes on the ground that these compounds are more "unsaturated."[19]

It is of interest to draw attention to the somewhat similar ideas which have been advanced to explain the mechanism of catalysis in organic reactions in ionising media. The reactive unit in the chemical change was taken to be a complex ion which the organic compound formed with an ion, generally the hydrogen or hydroxyl ion, of the catalyst (Lapworth, Bredig[20]); this additive compound is obviously analogous to the co-ordinative compounds, with which they may well be classed. In order to account for the abnormalities induced by the presence of salts, called the "neutral salt effect" by Arrhenius, in such reactions as are catalytically accelerated by acids and bases, the suggestion has been made that the non-ionised catalyst or the salt also forms a chemically active additive compound with one of the organic reactants; again this belongs to the more usual type of co-ordinative compound. This hypothesis, which has lately been vehemently advocated,[21] is claimed as giving values for the velocity-coefficients of such reactions more closely in accord with the experimental numbers than the theory that the hydrogen and hydroxyl ions are the sole agents in the catalysis. More fundamental and certainly as promising is Lapworth's[22] attempt to attack the problem of this type of catalysis by an investigation of the thermodynamic potential of such a catalyst as hydrogen chloride in alcoholic and aqueous alcoholic media; the hitherto inexplicable variation of the activity of this

[18] B. N. Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1089; *A.*, 1909, i, 897; *Chem. Zentr.*, 1910, ii, 378, 379; *A.*, 1911, i, 273; *J. Chim. Phys.*, 1911, **9**, 314; *A.*, 1911, i, 532; *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1329; 1912, **44**, 1113; *A.*, 1912, i, 100; ii, 922.

[19] Among others, P. Pfeiffer, *Annalen*, 1911, **383**, 92; *A.*, 1911, i, 788.

[20] *T.*, 1901, **79**, 1269; *Zeitsch. Elektrochem.*, 1903, **9**, 118.

[21] S. F. Acree, *Amer. Chem. J.*, 1913, **49**, 345; *A.*, ii, 576.

[22] W. J. Jones, A. Lapworth, and H. M. Lingford, *T.*, 1913, **108**, 252.

catalyst in a variety of reactions, when, for example, a small quantity proportion of water is added to an alcoholic medium, now becomes intelligible.

In the particular case of Friedel and Crafts' reaction it is difficult to harmonise the known facts with the hypothesis which gives to an intermediary co-ordinative compound the most important rôle in the condensation.[23] Apart from the great difference in the quantity of the catalyst demanded in different reactions, there is no relation between the vigour with which various chlorides react with hydrocarbons and their tendency to combine with aluminium chloride; some of the most reactive chlorides (carbon tetrachloride and chloroform) do not unite with the catalyst. Many acid chlorides, on the other hand, decompose easily under the influence of aluminium chloride; this sensitiveness is also apparently unconnected with the formation of additive compounds. The decomposition has been mainly studied in halogenated acid chlorides; the varying and sometimes devious course of the change is most readily understood on the supposition that a chlorine atom becomes loosened or detached. Occasionally the element is eliminated as free chlorine, or hydrogen and chlorine are simultaneously detached from adjacent carbon atoms.

Researches on the dynamics of Friedel and Crafts' and analogous reactions have not been particularly successful in elucidating the part played by the catalyst. The difficulties of accurate measurement are considerable. Using stannic chloride or ferric chloride, it was found that in the chlorination of benzene the speed was proportional to the concentration of the catalyst[24]; the chlorination of nitrobenzene and the benzylation of anisole in the presence of stannic chloride or aluminium chloride showed a similar relation.[25] A study of the interaction of *p*-bromobenzenesulphonyl chloride and benzene (and its derivatives) in the presence of aluminium chloride has, however, given more enlightening results.[26] These appear to show conclusively that this acid chloride at least is reactive only in so far as it is combined with the aluminium chloride; excess of acid chloride does not indeed enter into reaction. The accelerating effect of the aluminium chloride is, moreover, partly paralysed by excess of the product, the sulphone; hence it

[23] J. Böeseken and others, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 417; *ibid.*, 1911, **13**, 685; *A.*, 1910, i, 152; 1911, i, 173; *Rec. trav. chim.*, 1913, **32**, 1; *A.*, i, 334.

[24] A. Slator, *T.*, 1903, **83**, 729.

[25] H. Goldschmidt and H. Larsen, *Zeitsch. physikal. Chem.*, 1904, **48**, 424; *A.*, 1904, ii, 609. B. D. Steele, *T.*, 1903, **83**, 1470.

[26] S. C. J. Olivier and J. Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1069; *A.*, ii, 575.

may be concluded that the sulphone also combines with the catalyst. Notwithstanding the withdrawal of the aluminium chloride by union with these compounds, its general catalytic effect is but partly destroyed, for the speed of the reaction remains proportional to its total concentration. The free and not the combined aluminium chloride has, however, the most powerful action, as excess of aluminium chloride over the acid chloride effects a relatively very great acceleration of the condensation. The reaction cannot therefore be put down merely to the union of the catalyst with one of the reactants. It seems probable that this action is mainly exerted on the benzene; possibly it may be assumed that the catalyst acts by disturbing ("dislocating") the benzene molecule, so that the residual affinity becomes localised on one or more of the carbon atoms, either by forming a co-ordinative compound or by some more subtle influence falling short of a co-ordinative union. It is noteworthy that toluene, where the residual affinity would be less evenly distributed, reacts far more rapidly with the sulphonyl chloride than benzene.

The reaction may be represented as consisting of the following steps:

$$C_6H_4Br\cdot SO_2Cl,AlCl_3 + C_6H_6 = (I).\quad C_6H_4Br\cdot SO_2Cl,AlCl_3,C_6H_6 = (II).\quad C_6H_4Br\cdot SO_2\cdot C_6H_5,AlCl_3 + HCl.$$

Since the speed is proportional to the concentration of the aluminium chloride, it follows that reaction I is the slower change which is measured, whilst reaction II has a relatively high velocity, and hence is not measured. That the possession of residual affinity —an idea by no means of recent date [27]—confers the power to form co-ordinative compounds, and is closely associated with the catalytic activity of the aluminium chloride, can scarcely be doubted. This does not imply, however, that these additive compounds are the necessary intermediaries; their formation, in fact, involves a fall in potential, and hence a decrease in reactivity. The experimental evidence favours rather the view that the free aluminium chloride exerts some specific catalytic influence on the reactants. It is just when aluminium chloride forms a stable compound with one of these reactants that it is least effective, and hence a larger proportion is required to bring about a rapid reaction.

Keto-enol Isomerism. Reactivity of Tautomeric Compounds.

The rapid advance in the knowledge of keto-enol isomerism justifies a recent attempt [28] to revise the meaning of the various terms in common use. "Tautomerism" is to be used to include all

[27] H. E. Armstrong, *Proc. Roy. Soc.*, 1886, **40**, 285.
[28] K. H. Meyer, *Annalen*, 1913, **398**, 49; *A.*, i, 704.

compounds, which yield two series of substances derivable from two isomeric formulæ, when these formulæ differ only in the position of a hydrogen atom and of one or more ethylenic linkings. Tautomerism includes: (1) "Desmotropy," when the two unsubstituted isomerides can be shown to exist, for example, ethyl acetoacetate, ω-nitrotoluene, dianthronedi-imine; (2) "Pseudomerism," when only one form exists, the constitution of which can be exactly fixed. This "pseudomeride" can yield derivatives of the same constitution, or of the constitution of the isomeric "pseudo-form." Examples are anilines, phenols, oxymethylene compounds, and acid amides; (3) "Cryptomerism" denotes a tautomeric substance, existing only in one form, the constitution of which cannot be fixed with certainty. Examples are prussic acid, sulphurous acid, benzoquinoneoxime, sulphinic acids, and so forth.

Reactivity of Substances showing Keto-enol Tautomerism.—Although the reactivity of compounds showing this type of tautomerism is perhaps now more generally ascribed to the enolic form of the compound, since Lapworth's discovery of the mechanism of the bromination of acetone,[29] which has been so ingeniously utilised by Meyer as a test, the logical consequences of such view in its application to a number of organic reactions have not yet been accepted or even realised. The "addition-theory" of substitution generally, which owes much of its definiteness to A. Michael [30] and J. U. Nef,[31] finds far more adherents than the "substitution-theory," especially as it seems so particularly applicable to the Walden inversion, but evidence is nevertheless forthcoming that even in ketones direct substitution may take place. The optically active *o*-carboxy-2-benzyl-1-hydrindone yields the brominated ketonic acid,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CBr\begin{matrix}CH_2\\CO\end{matrix}>C_6H_4.$$

The enolic form of the hydrindone,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot C\begin{matrix}CH_2\\C(OH)\end{matrix}>C_6H_4,$$

contains no asymmetric carbon; hence if bromine only reacts with that, the product should be optically inactive. As a matter of fact, some 5—10 per cent. of the active compound is produced, mixed with much of the inactive. Obviously if the speed of enolisation were great, no active compound would appear, but the result

[29] *Ann. Report*, 1911, 101; *ibid.*, 1912, 125.

[30] *J. pr. Chem.*, 1888, [ii], **37**, 487; *A.*, 1888, 1054.

[31] *J. Amer. Chem. Soc.*, 1904, **26**, 1566; *A.*, 1905, i, 109. For a discussion of modern views on Substitution, compare W. P. Wynne, Presidential address to the Chemical Section of the British Association, 1913.

shows that bromination of ketones does not necessarily involve the intermediate formation of enol.[32]

A consideration of the most varied reactions of compounds capable of keto-enolic tautomerism[33] leaves little doubt that in general it is the enolic form that reacts. Even in the ketonic decomposition of β-ketonic esters,[34] which has now been found to take place quantitatively by simply heating with water at 200°, the speed of the reaction runs parallel with the readiness of enolisation, and becomes very slow in ketonic esters of the type:

$$\cdot CH_2 \cdot CO \cdot CRR' \cdot CO_2Et.$$

A comparison of the reactivity of enols and enolic ethers, and in particular of phenols and phenolic ethers, goes far in answering the question as to the cause of the peculiar reactivity of the enolic group.[35] The familiar theory which has again been recently advocated by O. Hinsberg[36] selects the ionisation of the movable hydrogen atom as the essential fact. It is now found, however, that the enolic ethers, $>C{:}C \cdot OEt$, are no less reactive than the enols; the essential feature is not the movable hydrogen, but the association of the oxygen atom with the ethylene linking, which gives rise to an "active double-linking," as the authors name it. As tests of reactivity the rates of reaction with alcoholic bromine, nitrous acid, diazo-solutions, and with aldehydes have been chosen. A comparison between the speeds of reaction of cinnamic acid and benzoylacetic acid (hydroxycinnamic acid), to choose a good example, illustrates well the enormous influence of the enolic grouping as contrasted with ordinary ethylenic linking. When the hydrogen is replaced by the ethyl group, as in ethoxycinnamic acid, there is no lessening of the speeds of reaction. The reactivity of the phenols is, of course, common knowledge, and is now shown to be comparable only to that of enolides, but it is not so well known that the phenol ethers are no less reactive. The authors emphasise the deduction that the phenols react as hydroxy-compounds, and not as ketonic pseudo-forms, as Thiele[37] and others have suggested. Moreover, in the analogous cases of anthranol and anthrone,[38] and of 9-phenyl-anthranol and -anthrone,[39] which are respectively desmotropes, the enolic form is alone reactive.

[32] H. Leuchs, *Ber.*, 1913, **46**, 2435; *A.*, i, 974.
[33] K. H. Meyer, *loc. cit.*
[34] H. Meerwein, *Annalen*, 1913, **398**, 242; *A.*, i, 858.
[35] K. H. Meyer and S. Lenhardt, *ibid.*, 66; *A.*, i, 723.
[36] *J. pr. Chem.*, 1911, [ii], **84**, 169; *A.*, 1911, ii, 873.
[37] *Annalen*, 1899, **306**, 122; *A.*, 1899, i, 873.
[38] K. H. Meyer, *ibid.*, 1911, **379**, 42; *A.*, 1911, i, 193.
[39] K. H. Meyer and A. Sander, *ibid.*, 1913, **396**, 133; *A.*, i, 489.

In the coupling with diazo-solutions there is but little difference in reactivity between the phenols and their ethers. The reaction is represented as primarily a simple addition (annexed formula), and on no ground requires the necessary formation of an intermediary oxygen–ether, $Ar{\cdot}N{:}N{\cdot}O{\cdot}Ar'$, examples of which have been recently isolated.[40]

In connexion with the reactivity of keto-enol tautomerides, reference should be made to the commonly supposed relation between the intensity of the selective ultraviolet absorption and the reactivity of the keto-enol form. The peculiarity of the absorption of enolides has recently been attributed by Hantzsch [41] to a static cyclic structure, rather than to a dynamic condition, and has found confirmation in some highly exact spectroscopic work.[42] Moreover, from a particularly searching experimental criticism to which this relation of absorption and reactivity has recently been submitted, it would appear not to be based on a correct interpretation of the known facts.[43]

That the "active double linking" is produced by the neighbourhood of the groups NH_2, NHR, and NR_2, as well as of oxygen, can be easily demonstrated in the pyrroles and indoles. The assumption that the reactivity of ("cryptomeric") pyrrole is associated with the tautomeric form, $N<\begin{matrix}CH{:}CH\\ |\\ CH{\cdot}CH_2\end{matrix}$, which possesses a so-called "reactive methylene-group," is not justified, inasmuch as *N*-ethylpyrrole, which can only exist in one form, is equally reactive; from analogy to the enolides it seems certain that the imino-form is the more reactive. The isolation for the first time of a desmotropic pair containing respectively an amino- and an imino-group is of particular interest in this connexion. The yellow, fluorescent diaminodianthryl,

$$NH_2{\cdot}C<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C{\cdot}C<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C{\cdot}NH_2,$$

and the colourless, non-fluorescent dianthronedi-imine,[44]

$$NH{:}C<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CH{\cdot}CH<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C{:}NH,$$

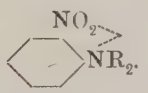
are analogous to the desmotropy of dianthrone and dianthranol, or to the as yet unknown desmotropy of aniline and its imino-form.

[40] O. Dimroth and M. Hartmann, *Ber.*, 1908, **41**, 4012; *A.*, 1909, i, 66.
[41] *Ann. Report*, 1912, 119, 123.
[42] P. J. Brannigan, A. K. Macbeth and A. W. Stewart, *T.*, 1913, **103**, 406.
[43] H. M. Dawson, *ibid.*, 1308.
[44] K. H. Meyer and H. Schlösser, *Ber.*, 1913, **46**, 29; *A.*, i, 295.

As a test of the constitution of enolides, ozone has recently been recommended, as it does not bring about a change of constitution [45]; by this means it is indicated that the enolide of benzoylacetone has the formula OH·CPh:CH·COMe,[46] since the ozonide yields on treatment with water, benzoic acid and methylglyoxal, and that of ethyl benzoylacetate in chloroform, mainly the constitution OH·CPh:C(COMe)·CO_2Et.

Nitro-compounds and the Quinonoid Structure.

Many attempts have been made in recent years, mainly by spectroscopic methods, to elucidate the exact constitution and to investigate the chromoisomerism of the nitroanilines.[47] In a very thorough discussion of the results, Hantzsch [48] concludes that the nitroanilines have not a quinonoid, as others had previously suggested, but a benzenoid structure, and, further, that the peculiarities of absorption and the chromoisomerism (or homochromoisomerism, when there is no difference in spectral characters) are to be attributed to the relations of one or more of the nitro-groups with the amino-group; this relation is expressed by a subsidiary valence:



Attempts to obtain chemical evidence have recently been made.[49] The mere fact that *o*- and *p*-nitroanilines dissolved in alcoholic alkali with a marked development of colour is evidence at least of some change, probably a quinonoid arrangement, in the salts, a view which has been generally accepted in the case of *o*- and *p*-nitrophenols.[50] The isolation of the potassium and sodium salts of a number of *o*- and *p*-nitroanilines gives point to this view; these salts, which are highly coloured and often exhibit chromoisomerism, in marked contrast to other similar salts, do not contain the elements of ethyl alcohol.[51]

[45] J. Scheiber and P. Herold, *Ber.*, 1913, **46**, 1105; *A.*, i, 490.

[46] Compare I. Smedley, *T.*, 1910, **97**, 1486.

[47] E. C. C. Baly, A. W. Stewart and W. H. Edwards, *ibid.*, 1906, **89**, 514; E. C. C. Baly, W. B. Tuck and E. G. Marsden, *ibid.*, 1910, **97**, 580; G. T. Morgan and A. Clayton, *ibid.*, 1911, **99**, 1945; G. T. Morgan, E. Jobling and R. T. F. Barnett, *ibid.*, 1912, **101**, 1209.

[48] *Ber.*, 1910, **43**, 1651, 1662; *A.*, 1910, i, 474, 475.

[49] A. G. Green and F. M. Rowe, *T.*, 1912, **101**, 2452; 1913, **103**, 508.

[50] H. E. Armstrong, *P.*, 1888, **4**, 27.

[51] For example:—M. Busch and M. Kögel, *Ber.*, 1910, **43**, 1549; *A.*, 1910, i, 472.

Recent spectroscopic work[52] on nitro-compounds and the nitrophenols might, however, suggest that these salts belong to the cyclic "conjugated" *aci*-nitro-type, with or without a quinonoid structure:

$$Ar\langle \begin{matrix} O \\ NO_2 \end{matrix} \rangle H \text{ (or M)}.$$

The spectroscopic evidence seems now fairly complete, at least for a change in the nitro-group and its relations in salt formation, if not as fully for a conversion of the benzenoid into the quinonoid configuration of the nucleus.[53] Moreover, the arguments in favour of a quinonoid structure gain considerably in force from the recent demonstration that the particular spectroscopic and colour changes occur only in the case of compounds where a quinonoid rearrangement is possible.[54] Nevertheless, the chemical evidence in favour of a quinonoid structure is extremely meagre, if not wanting. In recent literature there is much to suggest that the truism that the constitution can only be finally determined by chemical evidence, has been partly forgotten; spectroscopic and physical data in general point out analogies, and check the deductions from chemical investigations. The study of the reactions of salts of nitrophenols by Hewitt and his collaborators[55] is from this aspect very much to the point; the reactions of the group ·ONa in compounds of the type of sodium phenoxide have been shown to be wanting, and the reactions of the nitro-group to be modified, in the salts of nitrophenols. Hence it may be concluded that these salts contain neither the group :C·ONa nor the group :C·NO_2, but are derivatives of quinone–nitronic acids, to use Bamberger's apt name. The reactions chosen as tests were the condensation with ethyl chloroacetate, and the reduction to azoxy-compounds by sodium methoxide solution. The salts of *o*- and *p*-nitrophenols gave no response to either of these reagents, and in this respect stood apart from all the other phenols examined.

As an example of a spectroscopic investigation which has given exceptionally sure indications of the constitution of nitrophenols, the study of the absorption spectra of the derivatives of nitroaminophenols in neutral, acid, and alkaline solution is quite noteworthy.[56] The absorption under different conditions is sharply differentiated. In acid solution the absorption spectrum, for

[52] A. Hantzsch and K. Voigt, *Ber.*, 1912, **45**, 85; *A.*, 1912, i, 151; compare also G. T. Morgan and J. Reilly, *T.*, 1913, **103**, 1494.

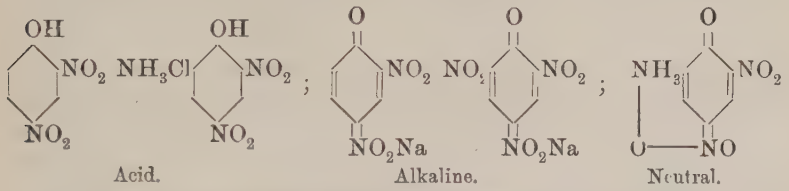
[53] *Ann. Report*, 1912, 118, 119, 120.

[54] J. T. Hewitt and others, *T.*, 1912, **101**, 1770.

[55] J. T. Hewitt, Miss R. M. Johnson and F. G. Pope, *ibid.*, 1913, **103**, 1626.

[56] R. Meldola and J. T. Hewitt, *ibid.*, 876.

example, of picramic acid, very closely resembles that of 2:4-dinitrophenol; on addition of alkali this spectrum changes to the "alkaline" type when the concentration of the hydrogen ions has dropped to 10^{-2}—10^{-3}. In neutral solution the curve more closely resembles the alkaline than the acid type. The structures in the various media are supposed to be as follows:



Acid. Alkaline. Neutral.

The absorption spectra have also been used to elucidate the nature of the peculiar isomerism of *o*-dinitrobenzidine [57]; it is deduced that the isomerism is to be attributed to both nuclei in one compound being quinonoid, whilst in the other one only has this structure.

Metaquinonoids.

Chemists seem less shy of using formulæ with a metaquinonoid linking than formerly, although the existence of undoubted examples of this type is by no means certain. Perhaps at the present time the salts of *m* nitrophenol would not be claimed as metaquinonoid,[58] whilst in other cases, for example, the so-called tribromoresoquinone,[59] the constitution was incorrectly assigned.[60] The yellow hydrocarbon, tetraphenyl-*m*-xylylene,[61] $C_6H_4<\begin{matrix}CPh_2\\CPh_2\end{matrix}$, which seems to be an undoubted *m*-quinonoid, has been prepared from methyl *iso*phthalate in exactly the same manner as the isomeric yellow *p*-compound was obtained from the terephthalate.[62] The absence of reaction with oxygen, and the inability to form additive compounds with ether, alcohol, and so forth, is taken to exclude the possibility of its being a triarylmethyl compound.

Chromoisomerism of Helianthine and Aminoazobenzenes.

A very interesting and illuminating example of the application of the freer ideas on valency, and of the delicate analysis by means of the

[57] *Ann. Report*, 1912, 120; J. C. Cain, A. K. Macbeth and A. W. Stewart, *T.*, 1913, **103**, 586.

[58] A. Hantzsch, *Ber.*, 1907, **40**, 339; *A.*, 1907, i, 207.

[59] C. Liebermann and E. Dittler, *Annalen*, 1873, **169**, 252; *A.*, 1874, 62.

[60] R. Meyer and K. Desamari, *Ber.*, 1908, **41**, 2437; *A.*, 1908, i, 658; *ibid.*, 1909, **42**, 2814; *A.*, 1909, i, 241, 657; *ibid.*, 1913, **46**, 1220; *A.*, i, 493.

[61] O. Stark and O. Garben, *ibid.*, 1913, **46**, 659, 2252; *A.*, i, 361, 849.

[62] J. Thiele, *ibid.*, 1904, **37**, 1463; *A.*, 1904, i, 491.

spectroscope, is to be found in Hantzsch's[63] study of the isomerism of methyl-orange (helianthine) and other aminoazobenzenes. It is now established that the solid, red helianthines, which can be isolated as mono- and di-alkylanilineazobenzenesulphonic acids, are dissolved by all indifferent media, and by alkalis as yellow helianthines, which have been isolated in the case of anilineazobenzenesulphonic acid. The "red" solutions are produced only in the presence of hydrogen ions, whilst the "yellow" appear always when this ion is absent, and not only when hydroxyl ions are present. The red salts have, without doubt, a quinonoid structure; spectroscopically they resemble very closely the rosaniline dyes in possessing the characteristic "quinonoid colour-band." The alkyl halogen derivatives of aminoazobenzenes,

$$Ar{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NR_2,CH_3X,$$

resemble spectroscopically azobenzene, and are undoubtedly benzenoid compounds; they may be termed "azonoid" salts. The yellow acid salts of dialkylaminoazobenzenes,

$$Ar{\cdot}N_2{\cdot}C_6H_4{\cdot}NR_2,HX$$

—in the case of helianthine, the internal sulphonate—which are generally unstable, are spectroscopically quite different from this class, and resemble closely the red salts and rosanilines; hence they are not "azonoid" salts, as was formerly stated.[64]

The suggestion that these salts are quinonoid by virtue of auxiliary valencies, that is, are "hemi-quinonoid," is negatived on account of the fact that the close spectroscopic resemblance to the red salts does not justify so great a constitutional difference. Hence it is concluded that the acid salts are also "holoquinonoid," and that chromoisomerism is to be attributed to valence-isomerism (2 and 3). A further consequence of this view is that free amino- and dialkylamino-azobenzenes, which show the quinonoid colour-band, must also be quinonoid in structure. Salt formation, then, is represented thus:

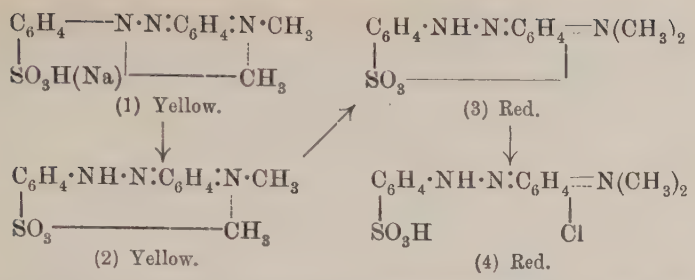
On the same grounds, yellow helianthines and alkaline solutions (methyl-orange) are also given a holoquinonoid structure (I).

The colour change of the indicator can therefore no longer be represented as the simple reversible transformation: azonoid salt $\rightleftharpoons$ quinonoid[65] salt, but is replaced by the following scheme:

[63] *Ber.*, 1913, **46**, 1537; *A.*, i, 775.

[64] A. Hantzsch, *ibid.*, 1908, **41**, 1172; *A.*, 1908, i, 469.

[65] J. T. Hewitt, *Analyst*, 1908, **33**, 85; *A.*, 1908, ii, 269; *T.*, 1909, **95**, 1292, A. Hantzsch, *loc. cit.*; H. T. Tizard, *T.*, 1910, **97**, 2477.



It will be noted that the quinquevalence of nitrogen in ammonium salts is given up in these formulæ for Werner's conception of a tervalent nitrogen linked to the acid by auxiliary valence.

This ingenious, if complicated, theory may perhaps express the facts more fully than the simpler ideas which it replaces, but it certainly does not seem to make plain why hydrogen ions convert the yellow solution of methyl-orange into the red.

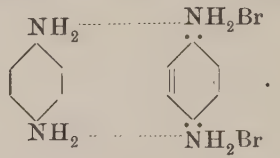
Some Researches on Colouring Matters.

The knowledge of the relation of the colour to constitution in some aromatic colouring matters has been considerably extended by some recent researches.[66] Piccard's examination of a number of *meri*-quinonoid salts derived from *N*-methyl- and *N*-phenyl-substituted *p*-phenylenediamines and benzidines has led to the conclusion that Nietzki's well-known rule must be modified. On increase of the magnitude of the molecule, the colour of a dye, according to Nietzki, passes up the spectrum, but, it has since been shown, at a certain point in the series of compounds returns again nearer to the red end. Since this behaviour has an analogy to the interference bands, in the colour of thin plates, and such-like, this second series is called the "absorption colours of the second order." Spectroscopic study indicates that the colours of the second order are distinguished by absorption in the red or ultra-red, as well as in the blue end of the spectrum. A colour of the second order is defined as that of a substance belonging to a homologous series of coloured compounds, the lower members of which have already passed through the usual colour series.

Very good examples of this phenomena are found in the *meri*-quinonoid salts obtained by oxidation of alkylated *p*-phenylene-diamines. The term *meri*-quinonoid is used for the intensely-coloured compounds of a quinone-hydrone type, which are completely stable towards water and alcohol, but cleft into their

[66] J. Piccard, *Ber.*, 1913, **46**, 1843, 1860; *A.*, i, 895, 896; F. Straus and A. Zeime, *ibid.*, 1912, **46**, 2267; *A.*, i, 992; E. R. Watson, *P.*, 1913, **29**, 348.

components by acids; to them is assigned formulæ in which the benzenoid and quinonoid parts of the molecule are connected by subsidiary valence definitely placed between the nitrogen atoms.[67]



The *holo*-quinonoid or the ordinary quinone-imonium salts possess one or more quinonoid nuclei, and are colourless or only feebly coloured. *meri*-Quinonedi-imonium bromide is yellow; successive substitution of the hydrogen atoms of the amino-group by methyl or phenyl groups causes a change of colour finally to blue in the diphenyl derivative; the colour of the tetraphenyl-*meri*-quinonoid salt is, however, green, and is therefore a colour of the second order. The *meri*-quinonoid derivatives from benzidine show this gradation even better; the unsubstituted compound is blue, whilst the tetraphenyl derivative is yellow of the "second order." In the di- and tri-phenylmethane series, numerous examples can be found; for instance, a series of blue and green dyes are derived from the salts of the benzhydrol, $NMe_2 \cdot C_6H_4 \cdot CH{:}C_6H_4{:}NMe_2Cl$, by replacement of the hydrogen of the central methane group by alkyl and other groups; but in auramine,

$$NMe_2 \cdot C_6H_4 \cdot C(NH_2){:}C_6H_4{:}NMe_2Cl,$$

an auxochromic amino-group replaces the chromophoric alkyl groups, and hence its yellow colour is of the second order. This suggestion is strengthened by the fact that reduction of the auxochromic action of the amino-group by acetylation is followed by a change of colour from yellow to blue of the "first order." Many anomalous relations in the colour of the diamino- and triaminotriphenylmethane series can be accounted for in a similar way; thus, malachite green, the tetramethyldiaminotriphenylmethane compound, corresponds with tetramethylmagenta, a tetramethyltriaminotriphenylmethane, the colour of which once more becomes green on acetylation of the amino-group; the colour of the malachite green is therefore of the first, and that of magenta of the second order.

The absorption spectra of various members of the triphenylmethane group have brought out some unexpected relations. It has been generally believed that only such quinonoid compounds of this group as possess an auxochromic group in the para-position to

[67] R. Willstätter and J. Piccard, *Ber.*, 1908, **41**, 1465; *A.*, 1908, i, 915.

the methane carbon atom, are dyes[68]; but the fact that fuchsone, $CPh_2{:}C_6H_4{:}O$, and benzaurin, $OH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O$, on the one hand, and fuchsonimonium chloride, $CPh_2{:}C_6H_4{:}NH_2Cl$, and the corresponding amino-derivative (Doebner's violet),

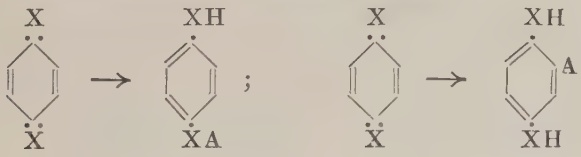
$$NH_2{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}NH_2Cl,$$

also yield similar absorption curves, makes this view untenable.[69]

Attention may be directed to a research[70] on the reduction of triphenylmethane dyes by formic acid to triphenylmethane, and ultimately to an aniline and a diphenylmethane; and to an extended series of experiments[71] on the action of ammonia and alkylamines on triphenylmethane dyes. The simple amine bases, $NHR{\cdot}CAr_3$, seem always to be the first product, but are in general more readily hydrolysed to the carbinol than the first examples of the type.[72]

The investigation of the benzoquinoneimine dyes has made clear a far-reaching similarity with those of the triphenylmethane series.[73] Safranine and the simpler indamine, $(NH_2Ph{\cdot}N{:}C_6H_4{:}NH)$, were chosen, and the changes of constitution accompanying change in the medium were mainly followed spectroscopically.

Mention should be made in this section of an interesting attempt[74] to refer the production of the many dyes, aniline black, indulines, nigrosines, etc., which are obtained in the oxidation of aniline, to two simple quinonoid reactions, namely, "direct addition" to an ethylene linking (I), and "indirect addition" (II). By action of the oxidising agent, these benzenoid products again become quinonoid, and condensation proceeds further.



(I.) (II.)

Lakes.—The investigation of the co-ordinative compounds, mainly of stannic chloride with the carbonyl group,[75] has led to the very

[68] A. von Baeyer, *Annalen*, 1907, **354**, 152; *A.*, 1907, i, 757. R. Meyer and O. Fischer, *Ber.*, 1911, **44**, 1944; *A.*, 1911, i, 723.

[69] R. Meyer and O. Fischer, *Ber.*, 1913, **46**, 70; *A.*, ii, 167.

[70] A. Guyot and A. Kovache, *Compt. rend.*, 1913, **156**, 1324; *A.*, i, 847.

[71] E. Noelting and J. Saas, *Ber.*, 1913, **46**, 952; *A.*, i, 522; compare E. Noelting and K. Philipp, *Ber.*, 1908, **41**, 579; *A.*, 1908, i, 295.

[72] V. Villiger and E. Kopetschni, *ibid.*, 1912, **45**, 2910; *A.*, 1912, i, 1030.

[73] F. Kehrmann, E. Havas and E. Grandmougin, *ibid.*, 1913, **46**, 2131; *A.*, i, 908.

[74] A. G. Green, *T.*, 1913, **103**, 925.

[75] *Ann. Report*, 1912, 139; P. Pfeiffer, *Annalen*, 1911, **383**, 92; *A.*, 1911, i, 788.

interesting discovery[76] of a series of substituted tin compounds or internal complex salts which are obtained by merely heating the former in solution or suspension in benzene, thus:

$$Cl_4Sn\begin{matrix}O{:}CR\cdot ArOH\\O{:}CR\cdot ArOH\end{matrix} = HCl + O{:}CR\cdot ArOH + \begin{matrix}RC{=}O\\|\\Ar\cdot O\end{matrix}\!\!>SnCl_3.$$

The co-ordinative compounds are only converted into complex salts when a hydroxy-group is in the ortho-position with respect to the carbonyl group. When there are two hydroxy-groups, such as in 2 : 4-dihydroxybenzophenone, a substituted derivative containing only one $SnCl_3$ is formed, whence it may be concluded that the ortho-placed hydroxyl group is alone involved. The co-ordinative compounds of some methyl ethers, as alizarin dimethyl ether, decompose in the same way, methyl chloride being evolved.

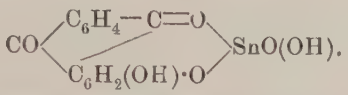
In this reaction of stannic chloride only with the *o*-hydroxyl group, the hydroxy-ketones show a remarkable contrast in their behaviour with bases. Only those hydroxy-ketones in which the hydroxy-group is in some other position than the ortho relative to the carbonyl group, such as 2-hydroxyanthraquinone, 2 : 6-dihydroxyanthraquinonone, alizarin, and so forth, form pyridine salts; moreover, the number of molecules of pyridine which combine with one molecule of the hydroxy-ketone are invariably less than the number of hydroxyl groups by the number of the ortho-placed hydroxyl groups. That the meta-hydroxyl group is more acidic than the ortho- is shown by the following facts: 2-hydroxyanthraquinone dissolves easily in 1 per cent. aqueous sodium carbonate, whilst 1-hydroxyanthraquinone does not; and alizarin and potassium acetate form the *m*-potassium salt.[77]

The absorption spectra of hydroxyanthraquinones also indicate some peculiar condition of the hydroxy-groups in the *peri*-position to the carbonyl, as the curve of the alkali salts of 1-hydroxy- is quite different from that of 2-hydroxy-anthraquinone; 1 : 4- and 1 : 5-dihydroxy- resemble a 1-hydroxy-anthraquinone in this respect.[78]

The inhibition of normal salt formation with the *o*-hydroxyl group is attributed to a relation (internal complex salt) existing between this group and the ketone, thus: $\begin{matrix}R\cdot C{=}O\\|\quad\diagdown\\C{-}O{-}H\end{matrix}$; this co-ordinative linking accounts for the conversion of the co-ordinative compounds with tin chloride into the substituted derivatives. These $SnCl_3$ derivatives of the *o*-hydroxyquinones are closely related

[76] P. Pfeiffer, *Annalen*, 1913, **398**, 137; *A.*, i, 879.
[77] W. H. Perkin, *T.*, 1899, **75**, 434.
[78] R. Meyer and O. Fischer, *Ber.*, 1913, **46**, 85; *A.*, ii, 168.

to the tin lakes, which contain no chlorine. The $SnCl_3$ derivative of alizarin in solution in pyridine is converted by water into a lake, which dyes silk and wool. It is suggested that the lakes have the constitution:

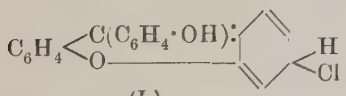


The relation is further emphasised by the fact that in dyes of the mordant class the hydroxyl group is always in the *o*- or *peri*-position to the chromophoric group.

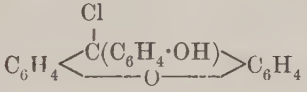
Triarylmethyl and Analogous Substances.

During the period under review a number of researches[79] have appeared which, although adding new members to this class, and removing some obscurities, have not done much to solve the mystery of their constitution or to harmonise the different views which have been expressed.[80]

In Gomberg's most recent publications, he still emphasises the quinocarbonium theory, and finds much additional evidence in the behaviour of the phenylxanthone salts,[81] which he maintains are carbonium salts, whereas Kehrmann claims them as oxonium salts.[82] In this series instances have now been obtained, when the coloured form, to which Gomberg ascribes the quinocarbonium form (I), is stable in the absence of excess of acid. The additional acid (or neutral salt) does not therefore cause the colour by uniting co-ordinatively with the colourless salt ("halochromy"), as Pfeiffer[83] has supposed. The presence of a hydroxy-group in certain positions, and to a less degree of a methoxy-group, are the favourable con-



(I.)



(II.)

ditions. This stability of the quinocarbonium salt is accompanied by a corresponding instability of the colourless benzocarbonium salt (II). Acetoxy- and benzoyloxy-groups have the opposite effect; the benzocarbonium salts are the more stable, and, moreover, the quinocarbonium salts, produced by addition of acids or salts, are

[79] W. Schlenk, *Ber.*, 1913, **46**, 1475, 1482; *A.*, i, 610. J. Schmidlin, *Ber.*, 1912, **45**, 3171, 3183, 3188, 3193, 3203; *A.*, i, 32, 33, 34, 46, 50. M. Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 200; *A.*, i, 257.

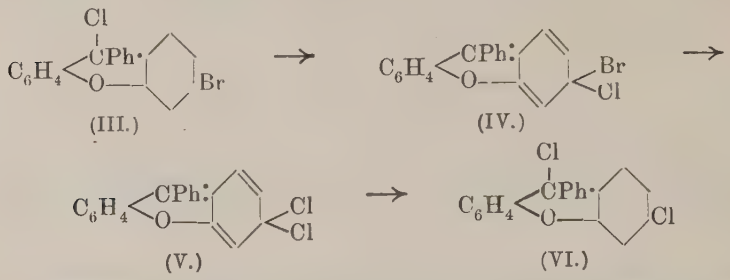
[80] *Ann. Report*, 1912, 139.

[81] M. Gomberg and C. J. West, *J. Amer. Chem. Soc.*, 1912, **34**, 1529; *A.*, i, 27.

[82] *Ann. Report*, 1912, 132.

[83] *Ibid.*, 139.

only faintly coloured. Striking evidence for the theory is found in the behaviour of the *p*-bromo-derivative:



(III.) (IV.) (V.) (VI.)

the *p*-bromobenzocarbonium chloride (III) yields a quinocarbonium salt (IV), which, however, passes back into a *p*-chlorobenzocarbonium salt (VI) with elimination of bromine.

The theory also gains greatly from the proof of the desmotropy of hydroxytriphenylcarbinols, which seems most simply accounted for as benzenoid-quinonoid tautomerism. The highly conflicting statements as to the properties of this compound which are found in the literature are thereby harmonised.[84]

The colourless form (m. p. 162—163°) separates from the alkaline solution on addition of ammonium chloride, and the yellow form (m. p. 139—140°) on acidifying with acetic acid. Each can be separately crystallised from appropriate solvents, but acid media convert the colourless into the coloured. Light effects the same transformation. Both desmotropes give the same red hydrochloride, $CPh_2{:}C_6H_4{<}^{Cl}_{OH}$, which is identical with that obtained from fuchsone, and is converted into fuchsone by molecular silver.[85]

The results of the many researches on the subject have led Gomberg to withdraw somewhat from his former position as to the relations and structure of triphenylmethyl, where he held that the bimolecular compound[86] contains a quinonoid nucleus, and is the only coloured form. He now suggests that the equilibrium represented below expresses best the behaviour of this compound.[87]

[84] A. Bistrzycki, *Ber.*, 1903, **36**, 2333, 3558; *A.*, 1903, i, 639; *A.*, 1904, i, 44. A. von Baeyer and V. Villiger, *ibid.*, 1903, **36**, 2774; *A.*, i, 811. K. von Auwers and O. Schröter, *ibid.*, 1903, **36**, 3236; *A.*, 1903, i, 820.

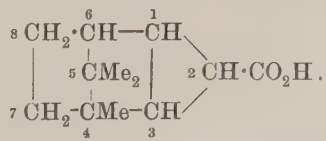
[85] M. Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 1035; *A.*, i, 1056.

[86] *Ann. Report*, 1912, 140.

[87] *Ber.*, 1913, **46**, 225; *A.*, i, 259.

Terpenes and Hydroaromatic Compounds.

The numerous recent additions to the polycyclic compounds, or compounds with "bridged rings," has led to several suggestions for extending and in part changing the present nomenclature.[88] The extension of von Baeyer's system for dicyclic compounds to tricyclic compounds, which has received von Baeyer's approval,[89] seems likely to prove immediately useful. Since each tricyclic system contains two tertiary or quaternary carbon atoms in the ring which are linked by bridges of carbon atoms, these bridges are selected as the central fact in the suggested nomenclature, and are represented by numbers, which also give the number of carbon atoms in the bridge. The series of numbers for the four bridges, which are always present in a tricyclic system, is called the "characteristic," except in completely symmetric formulæ it is necessary to distinguish the bridges further, by using as an index to the number of the "characteristic," the figure denoting carbon atoms from which a bridge starts or at which it ends. Unfortunately the numbering of the atoms in rings at present in use (Richter's "Lexikon," etc.) cannot be adapted to this system. It is suggested that a revised method of numbering should be adopted, in which, among other things, the numbering should always start from a quaternary (if possible) carbon atom at one end of the shortest bridge, and then always proceed clockwise round each bridge in turn. A fuller account is not possible here, but an example will illustrate the scheme: the bornylene derivative, shown in the annexed formula, is called 4 : 5 : 5-trimethyl*tricyclo*-[0, 1, $3^{4,6}$, 2]-octanecarboxylic acid:



The symbol $3^{4,6}$ refers to the bridge $>CH_{6}\text{-}CMe_{2}{}_{5}\text{-}CMe_{4}<$ between C^{1} and C^{3} from the carbon atoms, 4 and 6, of which the bridge, 2, springs.

Hydronaphthalenes.—The elegant method of preparing hydroaromatic hydrocarbons devised by Willstätter[90] has been used for

[88] V. Grignard, *Bull. Soc. chim.*, 1912, [iv], **11**, 124; *A.*, 1912, i, 177. A. Béhal, *ibid.*, 1912, [iv], **11**, 264; *A.*, 1912, i, 342; *Ber.*, 1900, **33**, 3775; *A.*, 1901, i, 135.

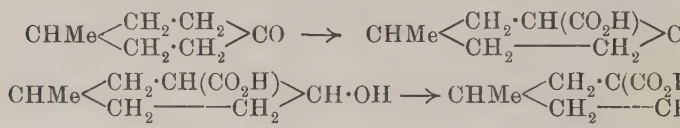
[89] E. Buchner and W. Weigand, *Ber.*, 1913, **46**, 2108; *A.*, i, 887.

[90] *Ann. Report*, 1912, 145.

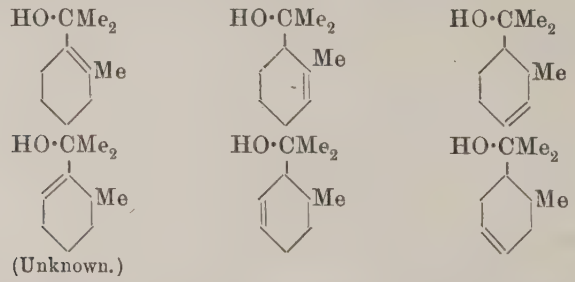
preparing dihydronaphthalene for the first time in a pure state[91] from *ac*-tetrahydro-β-naphthylamine.[92]

There seems to be some uncertainty as to the constitution of the dihydronaphthalene, for Straus and Lemmel[93] have converted Bamberger's Δ^2-compound into an isomeride, which they take to be the Δ^1-compound; moreover, it is stated that the Δ^1-dihydronaphthalene is exactly identical with the compound taken by Willstätter and King to be Δ^2-dihydronaphthalene.

Menthadienes and Menthenols.[94]—Great advances have been made in the synthesis of this important group of the monocyclic terpenes since an account was given in the Annual Reports (1910). In the *m*-menthadiene series (Reports, 1910) a great simplification of the synthesis of $\Delta^{3:8(9)}$-*m*-menthadiene[95] has been found in the preparation of 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid from 1-methyl-*cyclo*hexane-4-one; the series of transformations is shown in the following scheme; the carboxyl group is introduced by successive treatment with sodamide and carbon dioxide:



Of the *o*-menthadienes, of which no representative has yet been discovered in natural essential oils, five of the six possible menthenols and menthadienes have now been synthesised. The Δ^2-menthenol (Me = 1) and the corresponding menthadiene are alone unknown.



(Unknown.)

The syntheses of the ortho- resemble in general those used for

[91] E. Bamberger and W. Lodter, *Ber.*, 1887, **20**, 1706; *A.*, 1888, 292; 1896, i, 99.

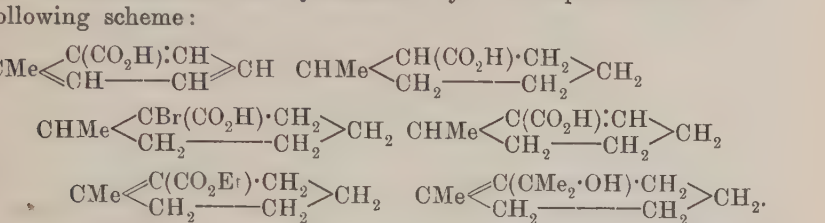
[92] R. Willstätter and V. L. King, *ibid.*, 1913, **46**, 525; *A.*, i, 353.

[93] *Ber.*, 1913, **46**, 232, 1051; *A.*, i, 256, 455.

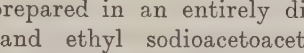
[94] A very lucid historical summary of syntheses in the terpene group was presented by Professor W. H. Perkin, jun., to the 8th International Congress of Applied Chemistry, VI, 224.

[95] B. D. W. Luff and W. H. Perkin, *T.*, 1910, **97**, 2147.

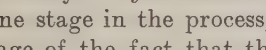
the para-series; starting from *o*-toluic acid, Δ^1-*o*-menthen-8-ol[96] and $\Delta^{1:8(9)}$-*o*-menthadiene are synthesised by the steps shown in the following scheme:



This pair was also prepared in an entirely different way from δ-acetobutyl bromide and ethyl sodioacetoacetate, which yield finally 1-methyl-Δ^1-*cyclo*hexenyl methyl ketone:



from which the menthenol is obtained directly by means of magnesium methyl iodide. 6-Hydroxy-*o*-toluic acid, which is itself prepared by fusion of naphthalene-1 : 3 : 5-trisulphonic acid with potassium hydroxide, is the starting point of the synthesis of Δ^5- and Δ^6-*o*-menthen-8-ol. The mixture of 1-methyl-Δ^5- and 1-methyl-Δ^6-*cyclo*hexene-2-carboxylic acids, which are obtained at one stage in the process, could only be separated by taking advantage of the fact that the Δ^5-acid esterifies, and the Δ^5-ester hydrolyses more rapidly than the corresponding Δ^6-compounds.

It is interesting to note in this connexion that a new terpene, crithmene,[97] has been isolated from *Crithmum maritinum* (Sardinia). A consideration of all its characters, including the fact that it yields a crystalline dihydrochloride, identical with that from terpinene, has led to the suggestion that it is $\Delta^{1:7—4:8}$-*p*-menthadiene,  , hitherto unknown.

*Dimethyl*cyclo*hexadienes.*—Exact knowledge of the dimethyl-*cyclo*hexadienes is yet in the main wanting. Some of the substances appearing under this heading in the literature can scarcely have the constitutions ascribed to them. The 1 : 4-dimethyl-$\Delta^{1:4}$-*cyclo*hexadiene, prepared by Auwers,[98] has been obtained in a pure state and accurately described Cantharene, obtained by Piccard from the natural cantharidine, was classed as an ortho-dimethyl derivative; it has now been shown to be 1 : 2-dimethyl-$\Delta^{2:6}$-*cyclo*hexadiene[99] by a very simple synthesis; 1-methyl-Δ^6-*cyclo*hexen-2-one (I) yields 1 : 2-dimethyl-Δ^6-*cyclo*hexen-2-ol (II), the

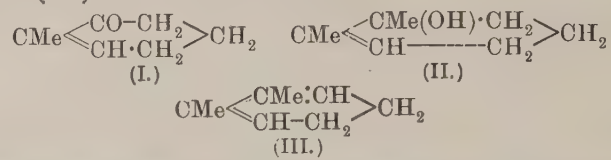
[96] W. H. Perkin, jun., and others, *T.*, 1911, **99**, 118, 518, 526, 727, 741.

[97] L. Francesconi and E. Sernagiotto, *Atti R. Accad. Lincei*, 1913, [v], **22**, i, 231, 312, 382; *A.*, i, 636.

[98] *Ber.*, 1908, **41**, 1816; *A.*, 1908, i, 520.

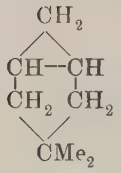
[99] W. N. Haworth, *T.*, 1913, **103**, 1242.

terpineol of cantharene series, which on dehydration passes into the hexadiene (III):



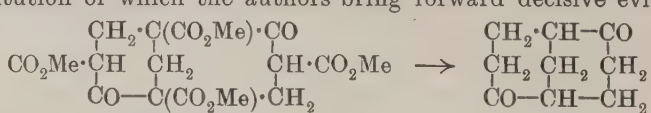
Although there is no doubt of the identity of the synthetic and natural hydrocarbon, the absence of crystalline additive halogen compounds makes comparison more difficult.

In a similar way 1 : 3-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene is prepared from 1-methyl-Δ^{1}-*cyclo*hexen-3-one.



Another interesting and simple synthesis[1] may be noted in that of 3 : 3-dimethyl*dicyclo*-[0, 1, 3]-hexane (annexed formula) from 1 : 1-dimethyl*cyclo*hexane-3 : 5-dione (dimethylhydroresorcinol); the ketone groups are reduced, the hydroxy-groups replaced by bromine, and then the two bromine atoms eliminated by zinc dust with formation of the trimethylene ring.

A remarkably simple synthesis of *dicyclo*-[1, 3, 3]-nonane derivatives[2] is worthy of note. Ethyl malonate and formaldehyde yield a mixture of methyl methylenemalonate and methyl methylenebismalonate and methyl pentane-$\alpha\alpha\gamma\gamma\epsilon\epsilon$-hexacarboxylate,[3] all of which are converted under the influence of sodium methoxide into methyl *dicyclo*-[1, 3, 3]-nonane-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate (I). The latter passes directly, or through a series of intermediaries, into *dicyclo*-[1, 3, 3]-nonane-2 : 6-dione (II), for the constitution of which the authors bring forward decisive evidence.



Camphene.—Fresh light has been thrown on the constitution of this hydrocarbon during the current year by some important researches. It would now appear that Wagner's formula (I) can alone represent reactions of the compound; and is now accepted provisionally by Aschan,[4] although this entails a profound transformation of the carbon skeleton during the oxidation by alkaline permanganate, when camphenic acid is formed.

[1] N. D. Zelinski and A. E. Uspenski, *Ber.*, 1913, **46**, 1466; *A.*, i, 607.

[2] H. Meerwein and W. Schürmann, *Annalen*, 1913, **398**, 196; *A.*, i, 869.

[3] W. H. Perkin, jun., and W. N. Haworth, *T.*, 1898, **73**, 330; W. H. Perkin, jun., and J. F. Bottomley, *ibid.*, 1900, **74**, 294.

[4] *Annalen*, 1913, **398**, 299; *A.*, i, 886.

Moreover, the fact that the oxidation both of bornylene and of camphene by hydrogen peroxide (in the latter case also by permanganate) yields camphenanic and *iso*camphenanic acids, suggests closer relation of the hydrocarbons than Wagner's formula indicates.[5]

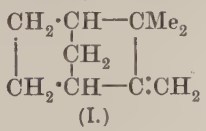
The reaction of camphene with ethyl diazoacetate (first used by Braren and Buchner[6] as a reagent with unsaturated cyclic hydrocarbons) yields 2 : 2-dimethylnorcamphane-3-*spirocyclo*propanecarboxylic acid (III), which gave on oxidation *cyclo*propane-1 : 1 : 2-tricarboxylic acid. If camphene possessed an endocyclic, as in Aschan's formula (II), instead of a semicyclic linking, *cyclo*propane-1 : 2 : 3-tricarboxylic acid would be the final product.[7]

In a similar manner bornylene and methyl diazoacetate react, forming methyl 4 : 5 : 5-trimethyl*tricyclo*-[0, 1, $3^{4,6}$, 2]-octane-2-carboxylate (formula, see p. 115), which on oxidation yields a *cyclo*propane-1 : 2 : 3-tricarboxylic acid. This behaviour is in accord with the usual formula for bornylene. The optical properties of these new derivatives of camphene and bornylene show the exaltation characteristic of tricyclic compounds.

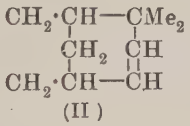
A reinvestigation[8] of the constitution of the compounds formed by the degradation of camphenic acid, on which the constitution of this acid was based by Aschan, has proved that Haworth and King[9] were right in their contention that Aschan had assigned an incorrect formula to the final product, a lactone-dicarboxylic acid. This acid has now been reduced to *iso*camphoronic acid, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, and hence is derived from a hydroxytricarboxylic acid of the formula:

$$CO_2H{\cdot}CH(OH){\cdot}CMe_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H.$$

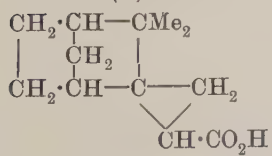
Since the lactone-carboxylic acid can also be converted into a stereoisomeride, it can only have the formula IV:



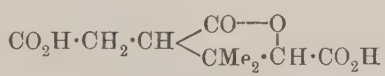
(I.)



(II.)



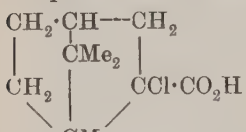
(III.)

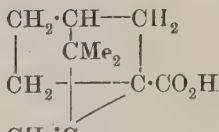


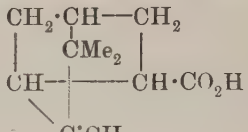
(IV.)

[5] G. G. Henderson and W. Caw, *T.*, 1913, **103**, 1543.
[6] *Ber.*, 1901, **34**, 982; *A.*, 1901, i, 385.
[7] E. Buchner and W. Weigand, *ibid.*, 1913, **46**, 759, 2108; *A.*, i, 376, 887.
[8] O. Aschan, *loc. cit.*
[9] *Ann. Report*, 1912, 149.

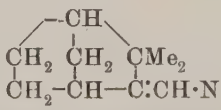
Collateral evidence in favour of Wagner's formula is found in the conversion of α-chloro*allo*camphanecarboxylic acid (I) into two isomeric camphanecarboxylic acids (II and III) by elimination of hydrogen chloride, a reaction quite analogous to the formation of camphene from bornyl chloride.[10] Further, it has now been


(I.)

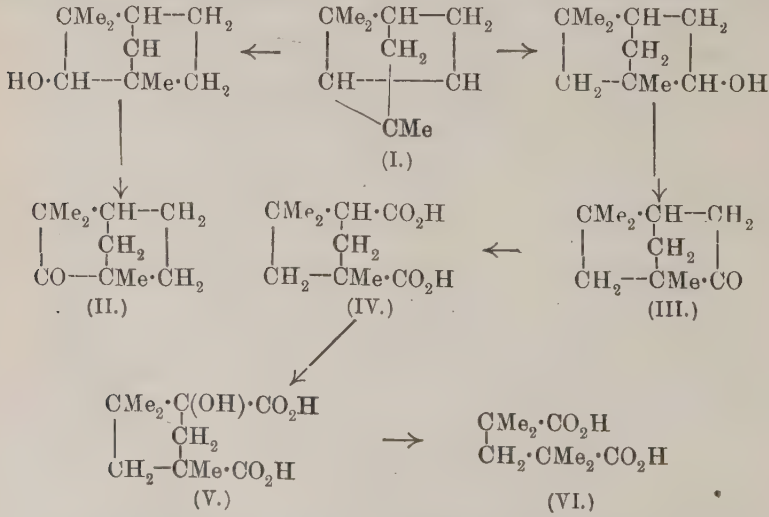

(II.)


(III.)

shown that nitrogen trioxide converts camphene into a nitro-compound, 1-nitrocamphene, which yields 1-camphenilone and nitromethane with alcoholic ammonia and camphenilanaldoxime, C_8H_{14}:CH·CH:NOH, on reduction.[11]



Fenchone and iso*Fenchone.*—Semmler's formula (II) for fenchone is now accepted by Aschan, and an analogous formula for *iso*-fenchone (III) suggested, as the constitution of *iso*fenchocamphoric acid (IV) has now been established by its conversion through hydroxy*iso*fenchocamphoric acid (V) to tetramethylglutaric acid

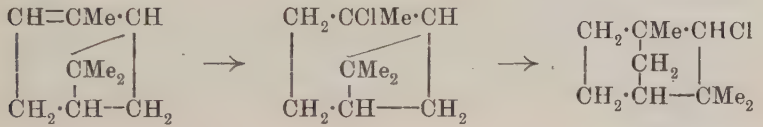

(I.) (II.) (IV.) (III.) (V.) (VI.)

[10] J. Houben and E. Willfroth, *Ber.*, 1913, **46**, 2283 ; *A.*, i, 970.

[11] W. Jagelki, *ibid.*, 1899, **32**, 1498. P. Lipp, *Annalen*, 1913, **399**, 241 ; *A.*, i, 1077.

(VI), which has been synthesised.[12] The relation of β-pinolene (I), renamed *cyclo*fenchene, to the fenchones is very simply explained by the reduction of the trimethylene ring, which is remarkably sensitive to acids, but stable to oxidising agents. The optical exaltation observed by Östling, moreover, provides additional evidence for this structure.[13]

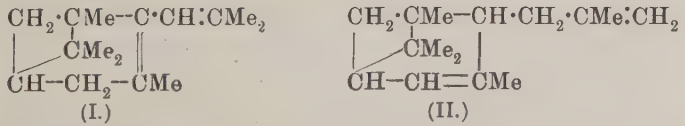
The conversion of pinene (I) into the fenchene-type of carbon-nucleus, which has been a difficulty in assigning formulæ, is now represented as but another instance of the pinacone-transformation, fenchyl chloride (II) being formed instead of the pinene hydrochloride:



(I.) (II.)

Fenchyl chloride, as pinene hydrochloride, reacts normally although not free from side-reactions with magnesium and carbon dioxide, yielding hydrofenchenecarboxylic acid; hydrodifenchene and hydrodifenchenecarboxylic acids are the main by-products.[14]

Caryophyllenes.—Although the reactions of this hydrocarbon, or rather mixture of closely allied hydrocarbons,[15] are such as to lead some observers to consider it a naphthalene derivative, Semmler[16] has now brought forward evidence which renders it more probable that the crude material consists of a mixture of two dicyclic sesquiterpenes, which are mutually convertible into one another. By careful oxidation, primarily by ozone, and by consideration of the physical constants of the products, the presence of a trimethyl-*cyclo*butane ring in each is demonstrated. The two hydrocarbons are named *terp*caryophyllene (I) and *lim*caryophyllene (II), from the analogy of the suggested structures to those of limonene and terpinolene respectively:



(I.) (II.)

[12] *Annalen*, 1912, **387**, 1; *A.*, 1912, i, 198. J. I. Michaelenko and W. P. Javorski, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 328; *A.*, 1900, i, 586.

[13] *T.*, 1912, **101**, 457.

[14] G. Komppa and S. V. Hintikka, *Ber.*, 1913, **46**, 645; *A.*, i, 375.

[15] C. W. Haarmann, *ibid.*, 1909, **42**, 1062; 1910, **43**, 1505; *A.*, 1909, i, 400; 1910, i, 496. E. Deussen, *ibid.*, 1909, **42**, 376, 680; *Annalen*, 1912, **388**, 136; *A.*, 1912, i, 368.

[16] F. W. Semmler, *Ber.*, 1911, **44**, 3657; 1912, **45**, 1384; *A.*, 1912, i, 120, 479.

Natural Products.

Caoutchoucs.—Harries'[17] researches on the rate of decomposition of the diozonides of natural and of the various forms of artificial caoutchoucs give the most exact means of discrimination yet discovered. The decomposition of "sodium" caoutchouc diozonides from isoprene and butadiene is quite different from that of natural, or the artificial "normal" caoutchoucs from isoprene or butadiene. Comparison of the decomposition curves of the diozonides of "normal" caoutchoucs ("normal" butadiene caoutchouc) and $\Delta^{1:5}$-*cyclo*octadiene shows a very remarkable similarity. The diozonides are also alike in the amount of succinaldehyde produced in the decomposition and in the want of response to hydrogen peroxide test. Harries is confidently of the opinion that "normal" caoutchoucs must contain an eight-ring of the type found in the octadiene.

The additive compounds of the caoutchoucs with the halogen acids are of the type $C_{10}H_{18}X_2$,[18] except that the synthetic caoutchoucs only combine with one molecule of hydrogen iodide. These compounds yield, on elimination of halogen acid, a material resembling artificial caoutchouc, but when sodium hydroxide is used instead of an organic base for this purpose, the material differs sharply in its inability to form ozonides.

It is suggested that the ethylenic linkings are conjugated in the eight-ring in the one case (I) whilst they are not in natural or "normal" caoutchouc (II), thus:

$$\left(\mathrm{CHMe}\begin{matrix}\mathrm{CH_2\cdot CH_2\cdot CH_2}\\ \mathrm{CH{=}CH\text{-}CH}\end{matrix}\mathrm{CMe}\right)_x \qquad \left(\mathrm{CMe}\begin{matrix}\mathrm{CH\cdot CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2\cdot CH}\end{matrix}\mathrm{CMe}\right)$$

(I.) (II.)

Carminic Acid, Kermes Dye, and Stick-lac Dye.[19]—This group of "insect" dyes, of which the best known is cochineal (carminic acid), have long defied the efforts of chemists to determine their chemical nature. They have now been shown to be anthraquinone derivatives, although Liebermann[20] had decided that such was not possible, since he failed to obtain anthracene from carminic acid by distillation with zinc dust.

Carminic acid, when pure, is now found to give a mixture of anthracene and methylanthracene. Carminic acid yields, on

[17] C. D. Harries, *Annalen*, 1913, **395**, 211, 264; *A.*, i, 284, 287.

[18] C. O. Weber, *Ber.*, 1900, **33**, 779; *A.*, 1900, i, 353; C. D. Harries, *Ber.*, 1913, **46**, 733; *A.*, i, 380. F. W. Hinrichsen, H. Quensell, and E. Kindscher, *Ber.*, 1913, **46**, 1283, 1287; *A.*, i, 637.

[19] O. Dimroth (with W. Scheurer and S. Goldschmidt), *Annalen*, 1913, **399**, 1, 43, 62; *A.*, i, 977, 980, 981.

[20] C. Liebermann and W. A. van Dorp, *ibid.*, 1872, **163**, 97; *A.*, 1872, 706.

oxidation with hydrogen peroxide, finally a compound which has been identified as 2 : 6-dihydroxy-8-methyl-α-naphthaquinonecarboxylic acid,

$$CO_2H\cdot C_6HMe(OH)\begin{cases}CO\cdot C\cdot OH\\ \|\\ CO\cdot C\cdot CO_2H\end{cases}.$$

The position of the hydroxyl groups is determined by the resemblance of this acid to 2 : 6-dihydroxy-α-naphthaquinone, which has been specially synthesised for the purpose.[21] On oxidation of the acid, carminazarin is produced, and has been shown to be 2 : 3 : 6-trihydroxy-8-methyl-α-naphthaquinone-5-carboxylic acid. By fusion with potassium hydroxide, carminic acid yields coccinin,[22] which is oxidised through coccinone to cochenillic acid (5-hydroxytoluene-2 : 3 : 4-tricarboxylic acid). Since both coccinin and coccinone give the characteristic colour reactions of hydroxyanthraquinones, it is suggested that their constitutions are represented by the formulæ:

$$C_6HMe(OH)_2\begin{cases}CO\cdot C\cdot CMe{=}{=}CH\\ \|\quad\quad\quad\ |\\ CO\cdot C\cdot C(CO_2H){:}C\cdot OH\end{cases}$$

Coccinone.

$$C_6HMe(OH)_2\begin{cases}C(OH)\cdot C\cdot CMe{=}{=}CH\\ |\quad\quad\ \|\quad\quad\ |\\ CH{-}{-}C\cdot C(CO_2H){:}C\cdot OH\end{cases}$$

Coccinin.

Carminic acid is then taken to possess this carbon skeleton (C_{14}); it is supposed that the five carbon atoms, which are lost in the alkali fusion, are arranged in a side-chain, and not as an additional fourth ring, as Liebermann suggested.[23]

Kermesic acid, the main constituent of kermes dye, is a simpler compound, the constitution of which is shown in the formula:

$$C_6Ac(OH)_3\begin{cases}CO\cdot C\cdot CMe{=}{=}CH\\ \|\quad\quad\quad\ |\\ CO\cdot C\cdot C(CO_2H){:}C\cdot OH\end{cases}.$$

Cochenillic acid can easily be obtained from it.

Laccaic acid, $C_{20}H_{14}O_{10}$, which is the main constituent of stick-lac dye, is not, as was formerly thought, identical with, but closely related to, carminic acid. Since it yields a series of derivatives, which closely resemble those obtained from carminic acid, and also give the colour reactions of 2 : 6-dihydroxy-α-naphthaquinone, there can be little doubt that it is also an anthraquinone derivative.

K. J. P. Orton.

[21] O. Dimroth and B. Kerkovius, *Annalen*, 1913, **399**, 36; *A.*, i, 979.

[22] H. Hlasiwetz and N. Grabowski, *ibid.*, 1867, **141**, 329.

[23] C. Liebermann and H. Voswinkel, *Ber.*, 1904, **37**, 3344; 1909, **42**, 1922; *A.*, 1904, i, 903; 1909, i, 486.

Part III.—Heterocyclic Division.

In drawing up a report in this section the main difficulty which its writer encounters is certainly not a lack of material. Yet even when the material is apparently plentiful the task of the reporter is not an easy one, for much of the work that is done does not lend itself to summarisation, whilst other portions of the field are so little investigated that the advance of our knowledge in them during the current year could only be expressed in the baldest form. Thus, on the one hand, there is a temptation to diffuseness which would end in a reproduction of the original papers practically verbatim; and on the other side there is the difficulty of avoiding a certain aridity in the style which would defeat the main object of the Reports. The present year has furnished examples of both these drawbacks.

From the point of view of the relation of chemistry to other sciences, the most important work has been carried out in the chlorophyll and hæmine groups; but the reasoning in this part of the subject is so intricate and the structures of the substances dealt with are so complex that it appears almost impossible to do more than touch on one or two points which appear of most importance; whilst others, which next year may appear of even greater interest, have perforce been sacrificed to lack of space and a fear of overloading one section of the Report.

Turning to other subjects, the progress of syntheses in the alkaloid group has not attained the same grade as was shown last year. In 1912 this section of the subject showed a very marked advance; but the present year has been devoted rather to the even more difficult work of determining constitutions by means of degradation reactions. Needless to say, this type of work is much more difficult to summarise than the other, for the results of a series of synthetic reactions can be expressed comprehensibly by means of formulæ with hardly any further explanation, whereas the views obtained by means of the degradation method can only be reproduced by a summary of reasoning which may be extremely difficult to condense without loss of clarity. Further, the results obtained by the method of degradation have always to be taken with a certain amount of reserve, as anyone who reads the back numbers of the Journals will have realised.

Among the synthetic heterocyclic substances the chief work of the year appears to have been carried out in connexion with indole and its derivatives, and our knowledge in this field has been considerably advanced. The cyanogen group also has received a certain amount of attention, and in this connexion the discovery

of carbon subnitride suggests that our knowledge of the cyanogen derivatives may be on the verge of a great extension.

The problem of residual affinity is being slowly elucidated, and it is not without interest to find that it is being attacked in the most widely-differing fields of the subject. In this way any possibility of a narrow outlook upon the question is automatically shelved, and it is to be hoped that more workers will enter this division of the subject.

Cyanuric Acid, Cyamelide and Ammelide.

Last year Chattaway[1] put forward a comprehensive explanation to account for the reactions of carbamide, cyanic acid, and other allied compounds. His view was based on the assumption that all the reactions dealt with were simply examples of the well-known tendency of the carbonyl radicle to add on groups such as R·NH·R or R·OH, this addition being followed by a wandering of a hydrogen atom from oxygen to nitrogen, as expressed by the following symbols:

$$\cdot N{:}C{:}O + H\cdot N{:} \rightleftharpoons \cdot N{:}C\!<\!\begin{matrix}OH\\N{:}\end{matrix} \rightleftharpoons \cdot NH\cdot CO\cdot N{:}.$$

The formation of cyanuric acid from carbamide may, on this hypothesis, be represented by the following formulæ:

$$NH_2\!\!\diagup\!\!CO\cdot NH_2 + OC(NH_2)_2 \longrightarrow NH\!<\!\begin{matrix}CO\cdot NH_2\\C(OH)(NH_2)_2\end{matrix} \longrightarrow$$

$$NH_3 + NH\!<\!\begin{matrix}CO\cdot NH_2\\CO\cdot NH_2\end{matrix} \longrightarrow NH\!<\!\begin{matrix}CO\cdot NH_2\\CO\cdot NH_2\end{matrix} + CO(NH_2)_2 \longrightarrow$$

$$NH\!<\!\begin{matrix}CO\cdot NH_2\\CO\cdot NH\cdot C(OH)(NH_2)_2\end{matrix} \longrightarrow NH_3 + NH\!<\!\begin{matrix}CO\cdot NH_2\\CO\cdot NH\cdot CO\cdot NH_2\end{matrix} \longrightarrow$$

$$NH\!<\!\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\NH_2\end{matrix} \longrightarrow NH_3 + NH\!<\!\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\!>\!CO.$$

This view has been criticised by E. A. Werner,[2] who has brought forward another explanation to account for the phenomena. According to him, cyanic acid is so unstable as to preclude its existence in unimolecular form, and it must also be assumed to be a mixture of two isomeric keto- and enol-forms. The enol-form tends to pass into the keto-form in the following manner:

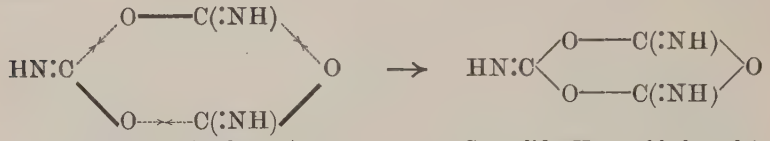
$$C\!\ll\!\begin{matrix}N\\OH\end{matrix} \longrightarrow C\!\ll\!\begin{matrix}N\uparrow H\\O\end{matrix} \longrightarrow \cdots C\!<\!\begin{matrix}NH\\O\end{matrix}\cdots \longrightarrow C\!\ll\!\begin{matrix}NH\\O\end{matrix}$$

Enol. Phase (*a*). Phase (*b*). Keto.

Since an interval of time must elapse while the hydrogen atom is migrating from oxygen to nitrogen, either a valency of the oxygen atom becomes momentarily free [Phase (*a*)], followed immediately by a momentary liberation of a carbon valency [Phase (*b*)]

[1] *T.*, 1912, **101**, 170. [2] *Ibid.*, 1913, **103**, 1010, 2275.

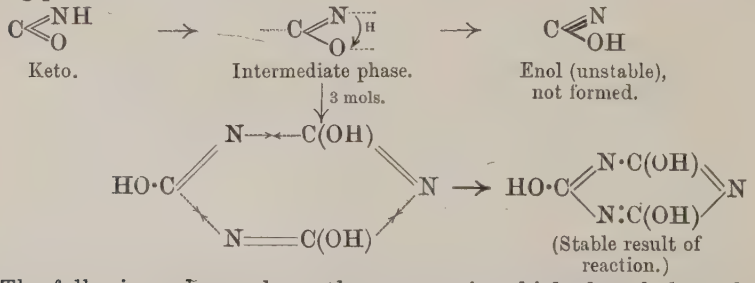
when the hydrogen atom unites with nitrogen, or, on the other hand, when the hydrogen atom has attained the position represented in phase (*a*) a simultaneous liberation of the respective valencies occurs, their union within the molecule giving rise to the keto-form of the acid. Since this is also taken as an unstable configuration it is concluded that the chief result will be the formation of cyamelide by the union of three molecules in phase (*b*), as shown below:



Three molecules in phase (*b*). Cyamelide (Hantzsch's formula).

According to this theory, cyamelide is not the result of the polymerisation of cyanic acid pre-existing in the keto-form, but is the product of the natural tendency to stable equilibrium formed whilst the acid is in the act of changing from one form to another.

Thus, on this theory, the prime condition for the production of cyamelide is that cyanic acid must exist in the enol form. At high temperatures, such as are found when carbamide is dissociated by heat, cyanic acid is assumed to be liberated in the keto-form, which at once polymerises to cyanuric acid, no cyamelide being produced:

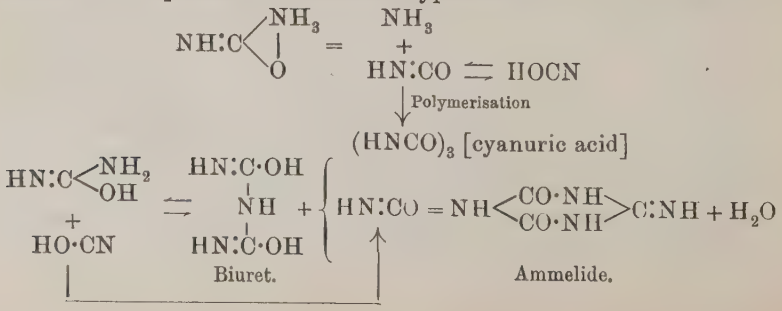


Keto. Intermediate phase. Enol (unstable), not formed.

3 mols.

(Stable result of reaction.)

The following scheme shows the manner in which the whole cycle of changes undergone by carbamide and biuret under the action of heat can be expressed on Werner's hypothesis:



Polymerisation

$(HNCO)_3$ [cyanuric acid]

Biuret. Ammelide.

A comparison of the two suggested explanations shows that they both depend on the formation of unstable intermediate stages, but that Chattaway assumes the formation of additive products, whilst Werner lays down the postulate that intramolecular vibration can be adduced to cover the ground. Werner's views certainly have the advantage of simplicity. At the present day the older idea that all reactions take place in two stages, first addition, and then decomposition, is coming once more into favour in some fields: and it seems probable that it will sooner or later be more generally combined with the dynamic conception of the molecule; so that the progress of all organic reactions will be ascribed, first, to intramolecular vibration resulting in the freeing of residual affinity, and secondly, to the formation of an unstable complex, which, by a rearrangement of affinity and possibly the elimination of certain atoms, passes into a third and stable condition. The study of such problems is at present possible only by physical means, such as refractometry or spectroscopy, and it would be interesting to see methods such as these applied to this problem. Meanwhile, the quantitative data which have been acquired in this region of chemistry are of great value from the theoretical point of view.

Carbon Subnitride.

A compound of considerable interest has been discovered during the year among the derivatives of carbon and nitrogen.[3] It has been obtained by heating tetraiodoglyoxaline, which loses three atoms of iodine at 180°, and parts with the last halogen atom when the temperature is raised to 420°:

$$\begin{matrix} CI\cdot NI \\ \| \\ CI-N \end{matrix}\!\!>\!C\cdot I \xrightarrow[-3I]{180^\circ} C_3N_3I \xrightarrow[-I]{420^\circ} C_3N_2.$$

When the heating process is carried out in such a way that no fusion of the substance occurs, the compound obtained resembles soot; but if the material is allowed to melt, the product has the appearance of the carbon which is obtained by the decomposition of sugar. Long heating renders the sooty substance hard and similar to graphite, with a colour varying between brownish-black and greyish-black. All forms are insoluble in indifferent solvents, and burn in a manner similar to charcoal; they have the property of absorbing gases, and they also are capable of removing colouring matters from sugar solutions.

With aqueous alkali or aqueous solutions of acid, neither ammonia nor hydrocyanic acid is liberated; but nitric acid attacks the substance with the production of carbon dioxide. When heated in a tube with soda-lime, ammonia is given off; whilst cyanogen is quantitatively produced when the substance is heated in a

[3] H. Pauly and E. Waltzinger, *Ber.*, 1913, **46**, 3129; *A.*, i, 1311.

stream of nitrogen. If the heating is carried out in an atmosphere of carbon dioxide, carbon monoxide and free nitrogen are formed, along with cyanogen.

In many respects the new substance appears to be allied on the one hand to paracyanogen, and on the other to animal charcoal. Its relation to paracyanogen appears in the method of preparation, for just as it is obtained by heating tetraiodoglyoxaline, so paracyanogen is prepared by heating cyanuric iodide above 200°[4]:

$$\begin{matrix} \mathrm{CI{\cdot}N{:}C\,I} \\ \| \quad\quad | \\ \mathrm{N{\cdot}CI{:}N} \end{matrix} \xrightarrow[-3\mathrm{I}]{\text{over } 200^\circ} \mathrm{C_3N_3}.$$

Both compounds when heated at high temperatures are almost completely decomposed into dicyanogen, although in the case of carbon subnitride one-third of the carbon remains behind in its elementary form. This reaction throws considerable doubt on the conception of paracyanogen as a polymeric form of cyanogen, for it seems more probable that both paracyanogen and carbon subnitride belong to a class of substances which liberate cyanogen as the result of some deep-rooted change in their constitutions under the influence of high temperatures.

In its relation to animal charcoal an even more striking similarity of properties is exhibited. Carbon subnitride, as was already mentioned, resembles animal charcoal in its physical properties; it has the power of absorbing gases just as charcoal does; it burns in a similar manner, and is equally insoluble in indifferent solvents. Both animal charcoal and carbon subnitride have the property of liberating ammonia on treatment with soda-lime; both substances yield cyanogen when heated to redness, but whilst carbon subnitride is completely dissolved by molten alkali, yielding hydrocyanic acid and carbon dioxide, animal charcoal is not thus soluble. It appears as if animal charcoal belonged to the same class of substances, but it is probably such an impure compound, as might be expected from its mode of formation, that it cannot show the exact behaviour of the pure carbon subnitride in its entirety.

It might be suggested that carbon subnitride was not a true compound, but merely a loose physical complex of carbon and nitrogen. The production of hydrocyanic acid from it on fusion with alkali tells against this hypothesis, as do the facts that its nitrogen content is not affected by pressure, and appears to be unchanged even over wide intervals of temperature. The fact that it contains more than 40 per cent. of nitrogen, whilst ordinary charcoal absorbs only about one-fifth per cent. of its own weight of nitrogen, appears to eliminate this hypothesis as to the nature of the nitride.

[4] P. Klason, *J. pr. Chem.*, 1886, [ii], **34**, 159; *A.*, 1886, 1001.

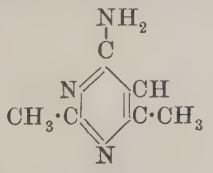
The intermediate product in the preparation of carbon subnitride is also of some interest. It has the composition $(C_3N_2I)_x$, and forms a sepia-tinted powder of the consistency of lampblack. It has no odour of iodine, is insoluble in all ordinary solvents and also in cold acids, but hot nitric acid attacks it with the formation of brown solutions and liberation of iodine. When heated with 15 per cent. potassium hydroxide solution it gives off no ammonia; but it dissolves in fused alkali, with the liberation of slight amounts of ammonia. Attempts to discover the exact position of the iodine atom in its structure by employing methyl derivatives of glyoxaline instead of the parent substance have so far proved fruitless.

It is too early yet to ascribe a structural formula to carbon subnitride, and it seems best to take for granted that the substance can be represented by the empirical formula $(C_3N_2)_x$. It appears probable that further investigation of this new class of substances, of which carbon subnitride and paracyanogen appear to be the only representatives yet obtained in a pure condition, will lead to very interesting results.

Antipyrinediazonium Salts and their Derivatives.

Although the vast majority of the diazo-compounds known at the present time belong to the aromatic series, there are a few isolated cases noted in the literature in which the diazotisable amino-group is attached, not to a benzene ring, but to a heterocyclic nucleus. A series of investigations [5] has been begun this year with the object of ascertaining within what limits the diazo-reaction is manifested by bases which do not contain amino-groups attached to aromatic nuclei.

It appears probable that if an amino-group is to be capable of diazotisation it must be attached to a nucleus containing an unsaturated group; but the converse proposition is not necessarily true, for cases are known in which an amino-radicle attached to an unsaturated group is not capable of forming diazo-compounds; for example, 6-amino-2:4-dimethylpyrimidine (cyanmethine), although it contains a cyclic system and an arrangement of valencies similar to that in benzene, behaves like an aliphatic amine, and does not resemble aniline in its powers of diazotisation:

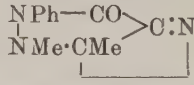


Cyanmethine.

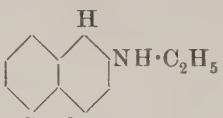
[5] G. T. Morgan and J. Reilly, *T.*, 1913, **103**, 808, 1494.

Several bases of the pyrazole series have been diazotised, and it has now been found that it is possible to isolate 1-phenyl-2 : 3-dimethylpyrazolone-4-diazonium chloride, which is produced by diazotising 4-amino-1-phenyl-2 : 3-dimethylpyrazolone (4-aminoantipyrine).

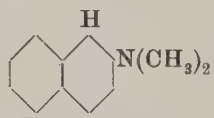
It is suggested that substances of this type may be of interest in connexion with the theory of the structure of diazo-compounds. If a co-ordination between the diazonium complex and the unsaturated ring be assumed, as some authors have proposed, then in the case of the antipyrine derivatives an analogous conjugation might be expected to take place. According to Morgan and Reilly, a general formula for these diazonium compounds might be represented by:



With regard to the reactions of these compounds it appears that a certain parallelism can be traced between their reactions with β-naphthylamine on the one hand and the β-diketones and β-keto-esters on the other. When two labile hydrogen atoms are present, condensation takes place; but when only one labile hydrogen atom is found in the compound the reaction does not follow the normal course; for example, the compound I couples with the diazonium derivative, whilst the substance II does not:

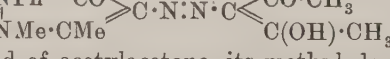


Couples.



Does not couple.

Acetylacetone can be coupled with the antipyrinediazonium compounds, yielding an azo-derivative of the following structure:



but when, instead of acetylacetone, its methyl derivative,

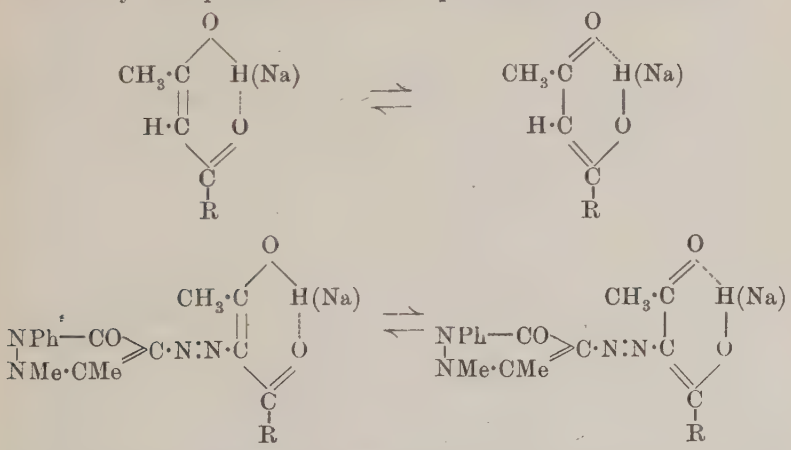
$$CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}CO{\cdot}CH_3,$$

is employed, the reaction is somewhat different. Coupling occurs, but it is accompanied by hydrolysis, resulting in the elimination of an acetyl radicle, and it seems probable that a compound of the type shown below is produced:

A study of the absorption spectra[6] of some of these substances

[6] The authors refer to some of their curves as "extinction" curves, but from the context it appears probable that they are ordinary absorption curves obtained by the usual qualitative method.

has been carried out, with interesting results. The case of ethyl acetoacetate will suffice to show the general nature of the data obtained. Ethyl acetoacetate in alcoholic solution shows no selective absorption. On coupling it with the antipyrinediazonium derivative, however, a substance is produced which has a well-marked absorption band in the region 2200—3200, with its head at 2600. The sodium derivative of the coupling product has an absorption spectrum practically identical with that of the azo-compound itself. Now it will be recalled that the addition of alkali to an alcoholic solution of ethyl acetoacetate results in the development of a band in the absorption spectrum of the substance, the head of the band lying at 3700. From these data Morgan and Reilly conclude that the antipyrineazo-compound has the same enolic structure as the β-diketone compound itself, and they further point to the results obtained in the case of the co-ordinated vanadium derivatives of diketones[7] in support of their view; and by this line of reasoning they come to the conclusion that there is a parallelism between the structures of the ordinary metallic derivatives of the diketones and those of the antipyrineazo-derivatives, which may be expressed in the two equilibrium formulæ below:



This involves, of course, the assumption that a band with its head at a frequency of 2600 units may be traced to the same origin as one which has its head at 3700 units, the difference being possibly ascribed to the very different molecular weights of the two substances.

The Alkaloids.

Last year was marked by a very rapid extension of our knowledge of the alkaloid group on the synthetic side, but during the

[7] G. T. Morgan and H. W. Moss, *T.*, 1913, **103**, 78.

present year the major part of the investigations has been directed toward the determination of the constitution of various members of the group by the usual process of degradation; thus the Report for the current year cannot seek to produce the same type of connected narrative which is possible when the final stages of synthetic work are concerned; but instead of this, all that is possible to do is to give a rapid survey of the various sections of the field, and draw attention to the general trend of the year's work.

Coniine, which has already given rise to a considerable amount of research, has again been pressed into service in the stereochemical field. Up to the present time only one case is known[8] in which two isomeric forms of a diquaternary ammonium salt containing two asymmetric nitrogen atoms have been isolated. It was thought that further progress might be rendered possible by employing a substance which, in addition to the nitrogen atoms, contained an asymmetric carbon atom also, and with this aim an attempt was made[9] to isolate all the possible forms of ethylenebis-*d*-coniine:

$$CH_2<\begin{matrix}CH_2\cdot CHPr^a\\ CH_2\text{---}CH_2\end{matrix}>N\cdot CH_2\cdot CH_2\cdot N<\begin{matrix}CHPr^a\cdot CH_2\\ CH_2\text{---}CH_2\end{matrix}>CH_2$$

When the nitrogen atoms in this substance are converted into quinquevalent ones by salt-formation, there are three possible isomeric forms which may be represented schematically by the following symbols, in which the plus and minus signs refer to the dextro- or lævo-configurations of the asymmetric atoms:

I. (N+,C+).....(N+,C+).
II. (N−,C+).....(N−,C+).
III. (N+,C+).....(N−,C+).

An attempt to obtain these has been only partly successful, two isomerides having been isolated, whilst the third possible isomeride has hitherto defied preparation. It is supposed that this unknown compound probably corresponds with the third configuration-possibility, and that under the conditions of experiment it is too unstable to exist, but passes into the configuration represented by the first formula.

In the quinoline group the work of the year has not been marked by any great advance in our knowledge, and a reporter must perforce confine himself to a brief mention of the various points which have been brought forward.

A simple method of preparation of hydroquinine esters has been worked out,[10] which depends on the action of hydrogen under

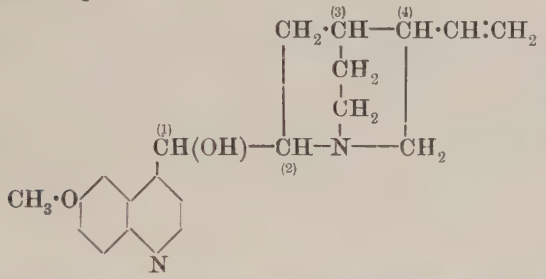
[8] E. and O. Wedekind, *Ber.*, 1910, **43**, 2707; *A.*, 1910, i, 834.

[9] E. Wedekind and F. Ney, *ibid.*, 1913, **46**, 1895; *A.*, i, 893.

[10] Vereinigte Chininfabriken Zimmer & Co., D.R.-P. 251936; *A.*, i, 85.

pressure in the presence of colloidal metals; for instance, when quinine ethyl carbonate, mixed with dilute sulphuric acid and a trace of colloidal palladium, is shaken in an atmosphere of hydrogen under pressure until no more hydrogen is absorbed, it is found that hydroquinine ethyl carbonate is formed. Some of these esters appear to have a therapeutic value.[11]

The investigations of Skraup and Koenigs in previous years have resulted in the conclusion that the alkaloids of the quinine series are all derivatives of a parent substance having the structure shown below, and, further, that these alkaloids may be classified into a series of pairs:



Chemically speaking, *l*-quinine closely resembles *d*-quinidine, and the other alkaloids of the group may be bracketed together in the following series: cinchonine–cinchonidine, hydroquinine–hydroquinidine, hydrocinchonine–hydrocinchonidine; thus there are four pairs of similar compounds in the group, and an examination of the formula will show that there are four asymmetric carbon atoms in it, numbered (1) to (4). It has been shown with regard to the atoms (3) and (4) that these have the same spatial arrangement in each of the eight alkaloids, and it therefore follows that the differences between the various pairs must be ascribed to the spatial arrangements of the atoms around the asymmetric carbon atoms (1) and (2).

Now if the hydroxyl group attached to the asymmetric atom (1) is replaced by a hydrogen atom it is found that (in the case of cinchonine and cinchonidine, for example) the end-products of the reactions are still different, for cinchonine gives rise to one particular product, whilst cinchonidine produces an isomeric substance. Since in the course of the reactions the asymmetry of the carbon atom (1) disappears, it is quite evident that this asymmetry cannot be the origin of the difference between the two compounds, and it seems very probable that the difference between them is to be sought in the different arrangements of the groups round the carbon atom (2).

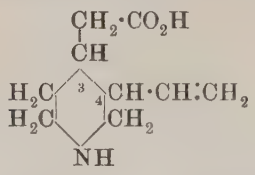
[11] Vereinigte Chininfabriken Zimmer & Co., D.R.-P. 253357; *A.*, i, 85.

On the other hand, if the secondary alcoholic radicle attached to the carbon atom (1) is oxidised to a carbonyl group, the asymmetry of the carbon atom (2) remains, on paper at least, just as little affected as in the case of the reduction of the hydroxyl radicle; yet in this case the end-products from cinchonine and cinchonidine are identical. To explain this it has been assumed that tautomeric change takes place as shown in the formulæ below, and that in this way the one form can pass into the other, so that it is impossible to isolate either substance in a pure form:

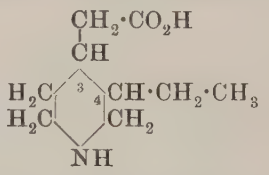
$$\cdot\overset{2}{C}H\cdot\overset{1}{C}O\cdot \rightleftharpoons \cdot\overset{2}{C}:\overset{1}{C}(OH)\cdot .$$

This view, however, leaves an important point out of consideration, namely, the bearing on the problem of the configuration of the groups associated with the asymmetric carbon atom (1).

Now all the alkaloids of the cinchona group yield on decomposition the same substance, meroquinonine (I), which can be reduced to cincholeupone (II), and from the study of the progress of the

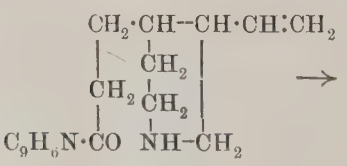


(I.)

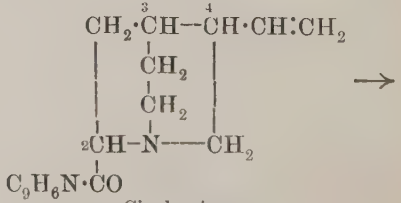


(II.)

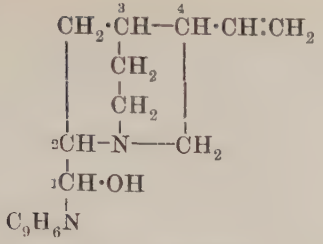
various reactions it appears that the spatial arrangement of the asymmetric atoms (3) and (4) remains unaffected through the decompositions. It remained to be proved, however, that, when the process was reversed and a synthesis of the alkaloid carried out, the configurations of the *four* asymmetric atoms would possess the configurations found in the natural alkaloids. Taking the formula of cinchotoxine to be that expressed below, it will be seen that its conversion into cinchoninone entails the production of the new asymmetric carbon atom (2), whilst the further step to cinchonine leads to the formation of the fourth asymmetric centre (1):



Cinchotoxine.

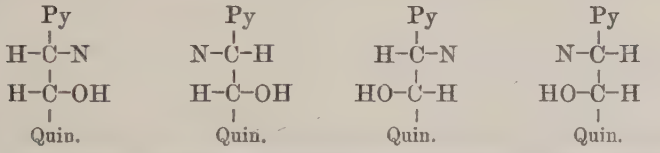


Cinchoninone.



Cinchonine.

When such a synthesis is carried out there are two possible courses before us. First, the asymmetry of the two carbon atoms (3) and (4) already present in the molecule may exert no influence on the mode of formation of the two new ones (1) and (2); or, secondly, owing to the presence of the asymmetric centres (3) and (4) there may be a selective formation of the new centres, such as is found in asymmetric syntheses. In the first case there will be a quantitatively equal yield of the four possible stereoisomerides in two pairs of antipodes, which can be represented by the formulæ below:



whilst the second postulate leads to the assumption that certain of the configurations will be favoured, and consequently there will be an unequal production of the various possible compounds in the reaction.

This theoretical view has been tested in the case of hydrocinchotoxine,[12] and it has been made reasonably certain that these synthetic processes do proceed in an asymmetric manner. Hydrocinchoninine, if it were an equimolecular mixture of two active compounds, would produce on reduction equal quantities of hydrocinchonine and hydrocinchonidine, but in actual practice it is found that the former substance is produced in 50 per cent. yield, whilst only 10 per cent. of the latter substance is found in the reaction mixture. The change of hydrocinchonicine, which contains two asymmetric centres, into an alkaloid with four asymmetric centres, proceeds asymmetrically, and it appears that of the four possible configurations those which are most favoured are those found among the natural alkaloids, hydrocinchonine predominating, whilst hydrocinchonidine is the next in the scale of formation.

[12] A. Kaufmann and M. Huber, *Ber.*, 1913, **46**, 2913; *A.*, i, 1222.

A study of the toxic effects of some synthetic compounds allied to the cinchona alkaloids has been made,[13] but the results obtained do not seem to lend themselves to summarisation.

In the morphine group the work of the year has been confined to one or two isolated investigations, chief among which appear to be the following. An examination of the crystalline character of codeine, narcotine, and other alkaloids derived from opium shows that they can be obtained in the superfused condition, as they can be caused to become solid without crystallisation taking place. They are all polymorphic, codeine having no less than five crystalline forms.[14] Attempts have been made to prepare a hydroxycodeine from aminocodeine by diazotisation, but the results do not appear to have been very definite.[15] A method of obtaining hydrogenised alkaloids of the morphine group by the action of hydrogen in the presence of colloidal palladium appears to work as well as the corresponding method in the case of the cinchona alkaloids.[16] Morphine glucoside has been prepared.[17] The formation of *apo*morphine in solutions of morphine which have been heated or allowed to remain has been investigated, and it appears that the change of one substance into the other does not take place.[18] An attempt has been made to synthesise *apo*morphine, but it was not successful.[19]

The syntheses of cotarnine and hydrastinine have been carried out in the following manner[20]: When homomyristicylamine formate is heated it yields formylhomomyristicylamine (I), which can be converted into norcotarnine (II) by the action of phosphoryl chloride and subsequent treatment with alkali:

$$CH_2{:}O_2{:}C_6H_2(OMe)\begin{cases}CH_2-CH_2\\ OCH{\cdot}NH\end{cases} \longrightarrow CH_2{:}O_2{:}C_6H(OMe)\begin{cases}CH_2-CH_2\\ CH=N\end{cases}$$

(I.) (II.)

The methiodide of this substance (II) is identical with the hydriodide of cotarnine. A similar method has been employed to produce norhydrastinine,[21] and from this substance hydrastinine and various homologues have been produced.[22]

A study of some condensation products of cotarnine has been

[13] A. Kaufmann, *Ber.*, 1913, **46**, 1823 ; *A.*, i, 763.
[14] P. Gaubert, *Compt. rend.*, 1913, **156**, 1161 ; *A.*, i, 643.
[15] F. Ferrein, *Arbeiten aus dem Pharmaz. Inst. Berlin*, **9**, 153 ; *A.*, i, 750.
[16] H. and B. Oldenberg, D.R.-P. 260233 ; *A.*, i, 1093.
[17] C. Mannich, *Annalen*, 1912, **394**, 223 ; *A.*, i, 87.
[18] M. Feinberg, *Zeitsch. physiol. Chem.*, 1913, **84**, 363 ; *A.*, i, 643.
[19] F. W. Kay and A. Pictet, *T.*, 1913, **103**, 947.
[20] H. Decker and P. Becker, *Annalen*, 1913, **395**, 328 ; *A.*, i, 290.
[21] *Ibid.*
[22] H. Decker, *Annalen*, 1913, **395**, 321 ; *A.*, i, 290.

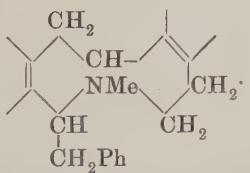
made, and the results are of considerable importance; the constitution of anhydrocotarnineacetophenone has been examined, and this substance has been shown to be an *iso*quinoline derivative.[23]

An investigation of the action of acetal on tetrahydropapaverine[24] has been carried out in the hope of throwing some light on the constitution of corydaline, but the results have not brought our knowledge very much forward. Instead of corydalines, the reaction appears to produce two other isomeric substances, which have been named coralydines, since they have the same composition as the corydalines, but differ from these in their properties.

The derivatives of dihydroberberine have been submitted to a very exhaustive examination, especially with regard to their behaviour when they are electrolytically reduced.[25] It is found that alkyl- or aryl-dihydroberberine derivatives react with methyl iodide to form the hydriodides of bases which are termed de-alkyl-(or de-aryl-)*N*-methyldihydroberberines. When reduced by the electrolytic method, each of the de-bases yields two reduction-products, *α*- and *β*-hydro-de-alkyl(or aryl-)*N*-methyldihydroberberines. The nature of the alkyl or aryl group appears to have no effect on the general character of all these compounds, so that it appears that the general constitution of the whole series is the same. From the fact that when the debenzyl derivative is oxidised it is converted into hydrastinine and 3 : 4-dimethoxy-2-styrylbenzaldehyde, the deduction is made that the debenzyl compound may be represented by the following formula:

$$CHPh{:}CH\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH\!<\!\begin{matrix}C_6H_2(:O_2:CH_2)\\ NMe\text{——}CH_2\end{matrix}\!>\!CH_2.$$

Against this, however, must be set the fact that the de-base cannot be reduced, nor does it react with bromine, and it seems possible that a better expression of the substance properties might be found by assuming that it contains a skeleton of the following type:



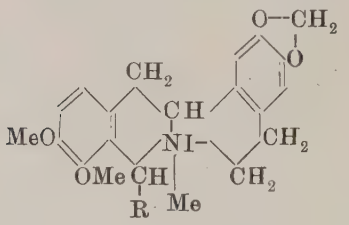
Two complete formulæ have been suggested for debenzyl-*N*-methyldihydroberberine, but it is admitted that neither of them is completely satisfactory.

[23] E. Hope and R. Robinson, *T.*, 1913, **103**, 361.

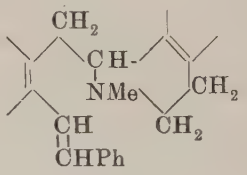
[24] A. Pictet and S. Malinowski, *Ber.*, 1913, **46**, 2688; *A.*, i, 1224.

[25] M. Freund (in conjunction with K. Fleischer, H. Commessmann, H. Hammel, D. Steinberger and E. Zorn), *Annalen*, 1913, **397**, 1; *A.*, i, 502.

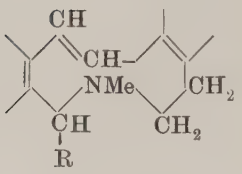
On reduction of the R-dihydroberberines (R being an alkyl or aryl radicle) it is found that each compound produces two stereoisomeric R-tetrahydroberberines, from which two stereoisomeric methiodides (I) have been prepared. These two methiodides when treated with silver oxide and subsequently with alkali, yield the same de-base. When R is a benzyl radicle the de-base probably has the formula II; if R is an *iso*propyl group the de-base has the structure III, whilst if R is a methyl, ethyl, *iso*amyl, *n*-octyl, or phenyl group, the de-base has the formula (IV):



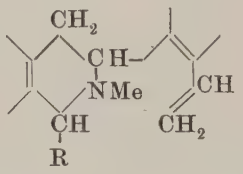
(I.)



(II.)



(III.)



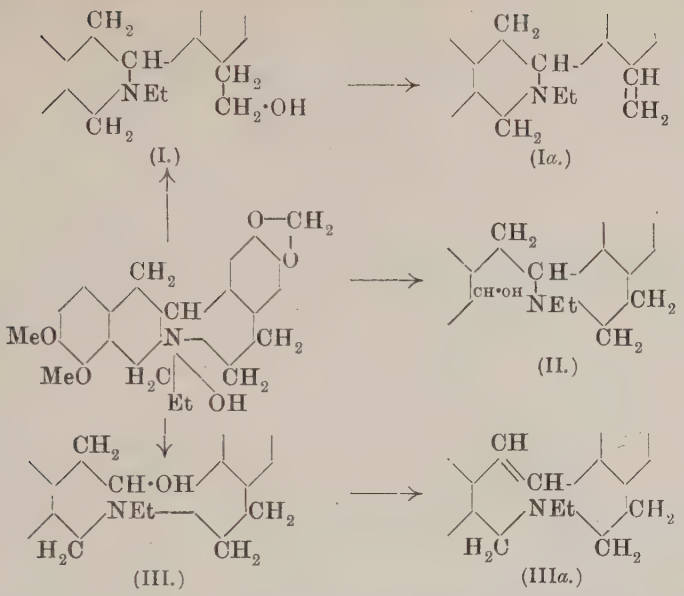
(IV.)

The conversion of berberine into hydrastinine[26] can be carried out in another way. On electrolytic reduction, phenyldihydroberberine yields two stereoisomeric phenyltetrahydroberberines, and when either of these is digested with silver chloride and subsequently reduced with sodium amalgam, it yields a base which on oxidation produces hydrastinine.

The constitution of the anhydro-bases derived from tetrahydroberberine presents another knotty problem. Tetrahydroberberine is a racemic compound, the lævo-isomeride of which is *l*-canadine. It was found by Voss and Gadamer[27] that the same optically inactive ethyl-anhydro-base can be obtained from either the racemic tetrahydroberberine or the optically active canadine. Now theoretically it is possible to obtain three hypothetical carbinol bases (I, II, and III) from tetrahydroberberine ethohydroxide, and of these (I) and (III) can lose water with the formation of the corresponding anhydro-bases (I*a*) and (III*a*) respectively:

[26] E. Merck, D.R.-P. 259873; *A.*, i, 1095.

[27] A. Voss and J. Gadamer, *Arch. Pharm.*, 1910, **248**, 43; *A.*, 1910, i, 415.



The formation of an inactive anhydro-base from *l*-canadine shows that this base must have the formula III*a*, since the other formula (I*a*) contains the original asymmetric carbon atom unchanged.

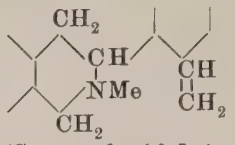
This conclusion has been criticised by McDavid, Perkin, and Robinson [28] on the ground that the formula III*a* contains a ten-membered ring and is therefore improbable.

In the present year the investigation has been carried further by the work of Pyman [29] on *l*-canadine. It was found that when *l*-canadine methohydroxide is evaporated to dryness in a vacuum a mixture of three anhydro-bases results, which have been termed A, B, and C respectively. When the corresponding racemic substance (tetrahydroberberine methohydroxide) is similarly treated only the two bases A and B are obtained, the third base not being found among the reaction products. A quantitative examination of the reaction products shows that the base A is formed in the same yield in both cases, whilst the yield of base B in the case of tetrahydroberberine is almost exactly equal to the combined yields of B + C in the case of the optically active canadine derivative. This suggests that B is the racemic form of C, and this hypothesis accounts for the fact that none of C can be detected when the starting material is the racemic tetrahydroberberine derivative.

With regard to the base C, Pyman concludes that it must have

[28] J. W. McDavid, W. H. Perkin, jun., and R. Robinson, *T.*, 1912, **101**, 1218.
[29] F. L. Pyman, *ibid.*, 1913, **103**, 817.

the following structure, which contains an asymmetric carbon atom:

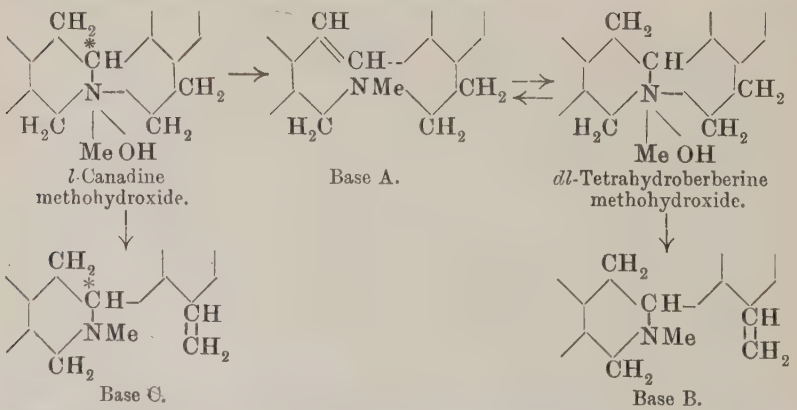


(Corresponds with I*a*.)

Since B, from evidence into which it is unnecessary to enter here, may be regarded as being the racemic form of C, it also has the formula I*a*. This leaves the constitution of the base A to be expressed by the formula III*a*, since there are only two possible formula open (I*a* and III*a*), and I*a* has already been appropriated for B and C.

Another point now arises. It was found that the production of the base A from either tetrahydroberberine methohydroxide or from *l*-canadine methohydroxide is a process which depends on certain experimental conditions; thus if either of the methoxides is evaporated to dryness under atmospheric pressure, no trace of the base A is produced. This has been traced to the fact that under these conditions the base A is unstable, and is converted into tetrahydroberberine methohydroxide, which, in turn, is changed into base B.

The whole course of the formation of the three anhydro-bases may be expressed in the scheme below [30]:



The constitution of aconitine [31] seems to be one of the problems which are nearing their solution. It appears to have the structure represented by:

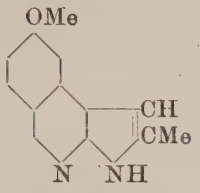
[30] The asterisks over the asymmetric carbon atoms indicate that the compounds are optically active.

[31] O. L. Brady, *T.*, 1913, **103**, 1821.

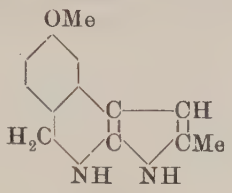
$$C_8H_7N\begin{cases}OAc\\OBz\\(CO_2H)_2\\(OMe)_2\\NO\\CH_3\end{cases}$$

so that it is now necessary to determine the constitution of the C_8H_7N nucleus.

It has now [32] been placed beyond doubt that the constitutions of harmine and harmaline are actually those suggested last year.[33]

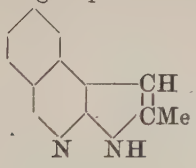


Harmine.

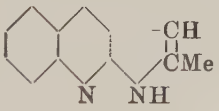


Harmaline.

The following is an outline of the proof. The methoxy-group is eliminated from the harmine nucleus by a series of reactions, into the details of which it is not necessary to enter. The resulting compound is termed harman. The point next at issue is to determine whether harman is a quinoline derivative or a member of the *iso*quinoline group. The two possible structures are *A* and *B*:

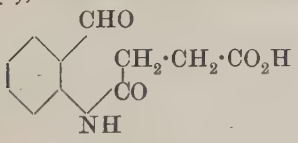


(*A.*)

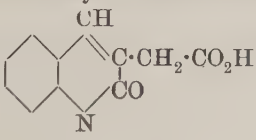


(*B.*)

In order to distinguish one from the other, it became necessary to produce synthetically a substance corresponding with one or other of the structures; and substance II was chosen. The usual indole synthesis was found not to be applicable when the benzene nucleus of indole is replaced by a quinoline ring; so recourse was had to another series of reactions. Condensation of *o*-aminobenzaldehyde with succinic anhydride produces *o*-aldehydosuccinanilic acid (I), which is then converted into carbostyril-3-acetic acid (II).



(I.)

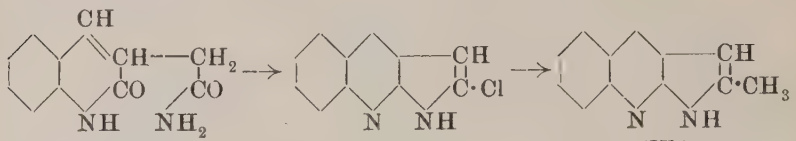


(II.)

[32] W. H. Perkin, jun., and R. Robinson, *T.*, 1913, **103**, 1973.

[33] *Ann. Report*, 1912, 159; *T.*, 1912, **101**, 1775.

The amide of this substance when boiled with phosphoryl chloride, undergoes a peculiar change, which results in the formation of chloronor*iso*harman (III):



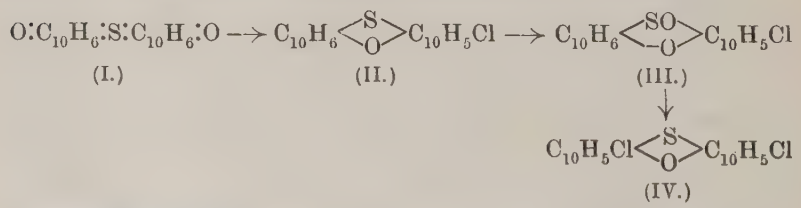
(II.) (III.) (IV.)

The Grignard reaction produces from this substance the corresponding methyl derivative (IV).

This substance was found to be isomeric with harman, and it is therefore termed *iso*harman. From this it follows that harman cannot have the quinoline structure *A*, but must contain an *iso*-quinoline nucleus corresponding with the formula *B* above.

The Naphthathioxins.

The investigation of the sulphides of β-naphthol, which was dealt with in last year's report,[34] has resulted in the discovery of a very peculiar case of isomerism.[35] It will be recalled that two isomeric forms of β-naphthol sulphide exist, and that, when they are dehydrated, each forms a peculiar naphthathioxin. The two naphthathioxins are not simply polymorphous substances, as they differ from each other in chemical properties to some extent, and each of them gives rise to a distinct set of derivatives. By the action of acetyl chloride on β-naphthasulphonium-quinone (I), monochloronaphthathioxin (II) was obtained. By converting this into the oxide (III) and subsequent treatment with hydrochloric acid, it was found possible to prepare dichloronaphthathioxin (IV):



(I.) (II.) (III.) (IV.)

Attempts were then made to prepare the same substances by the direct action of hydrogen chloride on the oxide of naphthathioxin, and mono- and di-halogen derivatives were actually obtained in this way. On examination, however, it was found that these new

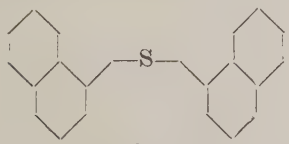
[34] *Ann. Report*, 1912, 160.

[35] T. J. Nolan and S. Smiles, *T.*, 1913, **103**, 340, 901; *P.*, 1913, **29**, 197.

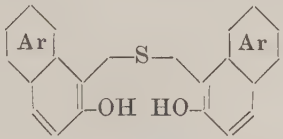
derivatives did not correspond with the substances prepared by the other method.

Two possible explanations of this phenomenon suggest themselves. In the first place, the differences observed may be due to structural isomerism arising from a difference in the positions of the chlorine atoms in the molecules; or, alternatively, there may be a difference betwen the two parental thioxins which persists in the derivatives. Evidence has now been brought forward which appears to exclude the first of these possibilities; and further investigation has shown that naphthathioxin actually exists in two isomeric forms, namely, naphthathioxin and *iso*naphthathioxin.

With regard to the constitutions of these two substances, the following data appear to be relevant. The molecular weights of the two isomerides measured in the same solvent are found to correspond with the simple molecular formula which results when a molecular weight of water is subtracted from two molecular weights of β-naphthol sulphide. The normal thioxin shows the usual character of substances of this class. The *iso*thioxin appears to contain the thioxin ring also. Further, it appears most probable that in both compounds this ring is attached to the naphthalene nuclei in the αβ-positions. From this evidence it appears that the skeletons of the two thioxins are similar; and the cause of the isomerism must be sought in the remaining portion of the molecule, namely, the naphthalene nuclei. This conclusion, however, is also applicable to the isomerism of the two sulphides of β-naphthol itself, since the properties of the two forms in which it occurs recall those of the two thioxins. It is suggested that in all these cases there is a difference between the distributions of affinity in the naphthalene nuclei which might be represented by the two formulæ below. The first formula may be taken as representing the true α-sulphide of β-naphthol, whilst II corresponds with the isomeric form which is obtained by the reduction of naphthasulphonium-quinone:



(I.)



(II.)

A similar idea was advanced by Collie,[36] who, from spatial considerations, concluded that it was probable that one of the naphthalene rings was olefinic in character, whilst the other was benzenoid, although under ordinary conditions it was possible that, owing to intramolecular vibration, each ring became olefinoid in turn.

[36] J. N. Collie, *T.*, 1897, **71**, 1017.

Willstätter and Waser[37] have also suggested something of the same kind. The phenomenon might be expressed thus:

It is not without interest that 3-phenanthrylamine[38] behaves to some extent like the naphthol derivatives. It occurs in two forms, one of which is obtained from the acetyl derivative of the other. Each substance gives a series of crystalline salts which, on decomposition, regenerate the isomeride from which they were produced.

There appears to be no doubt that further investigations in this line will widen our conceptions of the distribution of residual affinity within the molecule; and since the case of the sulphides of β-naphthol is evidently not an isolated one, it is to be hoped that any further examples of the same kind which are detected will be carefully investigated.

The Indole Group.

Reference to the literature betrays the fact that, whilst a very considerable amount of research has been carried out on the homologues of indole, the parent substance itself has been to a great extent neglected. The reason for this state of affairs must be sought in the fact that the hydrogen atom of indole is capable of changing its position from the nitrogen to the neighbouring carbon atom, and vice versa. The result of such tautomeric change is that when any reagent acts on indole the main reaction may be accompanied by one or more minor reactions which complicate the end-products. Further, the decomposition products obtained when the indole nucleus is attacked are very liable to undergo further changes which result in the formation of highly complicated compounds the constitutions of which are very difficult to ascertain.

To avoid this difficulty, some means must be found to fix the hydrogen atom and prevent intramolecular change during further reactions. Alkylation of the compound would accomplish this, but it would be practically impossible to remove the alkyl radicle at a later stage in the proceedings. The benzoyl radicle does not offer any such difficulty, as it can be attached to the nucleus with ease, and removed from it with equal readiness.

1-Benzoylindole[39] has been proved to be a most useful substance in this field; for by its aid the action of halogens on the indole

[37] R. Willstätter and E. Waser, *Ber.*, 1911, **44**, 3431; *A.*, 1912, i, 17.
[38] A. Werner and J. Kunz, *ibid.*, 1901, **34**, 2525; *A.*, 1901, i, 696.
[39] R. Weissgerber, *ibid.*, 1913, **46**, 651; *A.*, i, 387.

nucleus can be studied without any of the drawbacks which arise in connexion with the ordinary violent interaction between indole and the halogens. The reaction between the halogen and 1-benzoylindole is carried out in carbon disulphide solution, and yields of about 80 per cent. of the theoretical are obtainable. The benzoyl derivative is then hydrolysed by means of ammonia, and in this way the pure indole halogen substitution product is obtained.

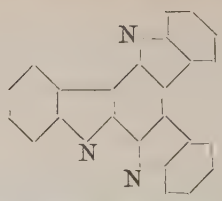
The same substance has been employed in order to produce a reaction which has hitherto been unattainable in the parent indole. It is well known that in the indole homologues it is possible to open up the pyrrole ring in such a way as to produce derivatives of anthranilic acid; but when oxidising agents are applied to indole itself the reaction-products are by no means so simple as is the case with the homologous compounds. It has been found, however, that 1-benzoylindole can be oxidised in acetone solution by means of permanganate with the production of benzoylanthranilic acid, which can easily be hydrolysed to its parent substance.

A study of the action of ozonised air on solutions of the salts of 2- and 3-indolecarboxylic acids has been made; and it appears that the 2-acid is not markedly affected, whereas the 3-acid produces a good yield of indigotin. The rapidity of the action is sufficiently great to allow the experiment to be used for lecture demonstration purposes.

In the distillation of large quantities of nearly pure indole, it is found that a small quantity of a product of high boiling point is left behind in the distilling flask. An examination of this substance[40] shows it to be a trimeric form of indole. It might have been expected, from analogy to pyrrole, that tri-indole could be prepared by the action of condensing agents on indole, but experiment has shown that this is not the case, for no characteristic compound is produced in these circumstances.[41] Tri-indole is of some interest in certain of its characteristics. On distillation in a vacuum it gives a quantitative yield of indole; acetic anhydride produces a monoacetyl, benzoyl chloride a monobenzoyl derivative. Benzoyltri-indole, when heated in a vacuum, decomposes into indole and benzoyldi-indole. These acyl derivatives of the indole series are apparently *N*-derivatives, for the acid radicles cannot be removed from them by the action of the usual hydrolytic agents. Several formulæ might be suggested for the structure of tri-indole, but the one that appears most satisfactory in view of its reactions is the following:

[40] K. Keller, *Ber.*, 1913, **46**, 726; *A.*, i, 403; see also B. Oddo, *Gazzetta*, 1913, **43**, i, 385; *A.*, i, 755, and M. Scholtz, *Ber.*, 1913, **46**, 1082; *A.*, i, 520.

[41] See, however, M. Scholtz, *ibid.*, 1082; *A.*, i, 520.



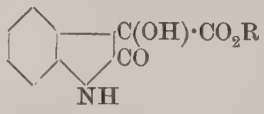
Further investigations have been made during the year on the reactivity of the β-unsubstituted pyrrole ring.[42] It will be recalled that a fairly close parallelism seems to exist between the 3-unsubstituted indole derivatives on the one hand and the primary aromatic amines and the phenols on the other.[43] It has now been shown that the 3-unsubstituted indoles react with pyridine and cyanogen bromide, yielding dyes which have the general formula:

$$NH<\begin{matrix}C_6H_4\\ \\ CR\end{matrix}>C\cdot CH:CH\cdot CH:CH\cdot CH:C<\begin{matrix}C_6H_4\\ \\ CR\end{matrix}>NHX.$$

These substances are closely allied to the pyridine dyes which can be obtained from the aromatic amines.

A new method of obtaining substituted indole derivatives[44] has been discovered, which depends on the action of heat and a catalyst, such as cuprous chloride or zinc chloride, on the hydrazones of aldehydes and ketones. For example, when methyl ethyl ketone-phenylhydrazone is heated to 180—230° in the presence of a trace of cuprous chloride, a 60 per cent. yield of 2 : 3-dimethylindole is produced.

Another method of obtaining indole derivatives is based on the condensation of primary and secondary aromatic amines with the esters of mesoxalic acid.[45] Aniline yields an ester of dioxindole-3-carboxylic acid:



which can be saponified with aqueous potassium hydroxide in the absence of air with the production of dioxindole. This last substance, if left exposed to air in an open vessel, is rapidly oxidised to isatin. Other aromatic amines yield the corresponding products.

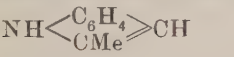
The synthesis of indole itself has been accomplished in a somewhat roundabout manner, starting from *o*-toluidine.[46] The amine is converted into the oxalo-derivative, and then fused with some sub-

[42] W. König and R. Schreckenbach, *J. pr. Chem.*, 1913, [ii], **87**, 241; *A.*, i, 400.
[43] W. König, *ibid.*, 1911, [ii], **84**, 194; *A.*, 1911, i, 808.
[44] A. E. Arbuzov and V. M. Tichvinski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 70; *A.*, i, 388.
[45] A. Guyot and J. Martinet, *Compt. rend.*, 1913, **156**, 1625; *A.*, i, 756.
[46] W. Madelung, *Ber.*, 1912, **45**, 3521; *A.*, i, 91.

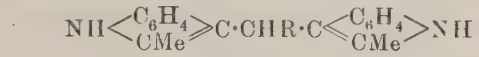
stances, such as barium hydroxide, which have the property of acting as alkaline condensing agents without producing hydrolysis of the acyl derivatives. In this way an indolecarboxylic acid is produced, which, on distillation, decomposes into the parent substance.

The reactions of the methyl radicle when directly attached to an aromatic or heterocyclic nucleus are of great importance from the point of view of the problem of residual affinity; for it is well known that such methyl radicles possess many properties which bring them into line with the methyl group of an acetyl radicle. Further accumulation of facts in this field is much to be desired; and those which have come to light during the year are of no little interest.

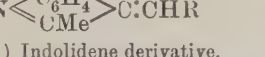
In the case of 2-methylindole, the methyl group appears to be very sensitive to the conditions under which the reaction is carried out, for example, when an aldehyde is allowed to react with 2-methylindole in neutral or acidic solution, a di-indylmethane derivative (I) is formed,[47] whilst in a strongly acid, alcoholic solution the end-product is an indolidene compound (II).[48]



2-Methylindole.



(I.) Di-indylmethane derivative.



(II.) Indolidene derivative.

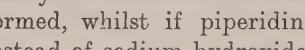
It has been found[49] that when compounds containing the grouping $-CH_2\cdot CO\cdot CH_3$ are allowed to react with aromatic aldehydes under the influence of condensing reagents, the reactions are influenced by the nature of the solvent. In alkaline solution the methyl radicle is attacked by the aldehyde, whilst in acid solution it is the methylene group that is acted on. Now in 2-methylindole there is no carbonyl radicle, but instead of it there is an ethylenic bond; and the question suggests itself whether the reactions of 2-methylindole lend any countenance to the idea that there is a parallelism between the groupings $-CH_2\cdot CO\cdot CH_3$ and $-CH{:}C\cdot CH_3$. The actual experimental results do not tend to support this view. In alkaline solution, the methine group of 2-methylindole reacts with aldehydes, but the reaction is not similar to the normal reaction between an aldehyde and a methyl radicle; for it is found that the alcohol which is used as a solvent plays a

[47] E. Fischer, *Ber.*, 1886, **19**, 2988; *A.*, 1887, 265.

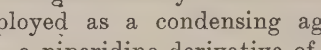
[48] M. Freund and G. Lebach, *ibid.*, 1905, **38**, 2640; *A.*, 1905, i, 663; C. D. Harries and G. H. Müller, *ibid.*, 1902, **35**, 966; *A.*, 1902, i, 295.

[49] M. Scholtz, *ibid.*, 1913, **46**, 2138; *A.*, i, 893.

part in the reaction, giving rise to a compound of the type I. With methyl alcohol as a solvent, the analogous methyl derivative is formed, whilst if piperidine is employed as a condensing agent instead of sodium hydroxide solution, a piperidine derivative of the type II is produced:

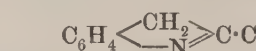


(I.)



(II.)

When formic acid is allowed to react with 2-methylindole, the former substance behaves as if it were an aldehyde, but the reaction appears to take place in two stages. In the first phase, the indole derivative reacts in the indolenin form:



and the two hydrogen atoms of the methylene radicle are removed along with the oxygen atom of the formic acid carbonyl group. The second phase of the reaction is brought about by the interaction between another molecule of 2-methylindole and the hydroxyl group of the formic acid residue in such a way as to produce 2-methylindolyl-2-methylindolidenemethane:

A curious anomaly is shown when *o*-nitrobenzaldehyde is used instead of the other aromatic aldehydes. Instead of the normal condensation, a reaction takes place which to some extent recalls aldol formation, with the result that a compound of the following type is produced:

It might be supposed that such a deviation from the normal course might be due to the influence of the ortho-substitution of the aldehyde; but examination has shown that salicylaldehyde and *o*-chlorobenzaldehyde both react in a manner exactly similar to benzaldehyde, which, of course, proves that ortho-substitution is not the real cause of the deviation of the nitro-compound from the normal.

When, instead of aldehydes, ketones[50] are condensed with 2-methylindole, the results are quite different, for the reaction follows another course; for example, when acetone is allowed to act on 2-methylindole under the influence of hydrochloric acid, the following compound is produced:

[50] M. Scholtz, *Ber.*, 1913, **46**, 1082; *A.*, i, 520.

This reaction also is very sensitive to any change in the conditions under which it is carried out; thus if glacial acetic acid is substituted for the hydrochloric acid, the reaction product is:

$$NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot CMe_2\cdot C<\begin{matrix}C_6H_4\\CMe\end{matrix}>NH.$$

Methyl ethyl ketone behaves like acetone, but when an attempt was made to utilise diethyl ketone it was found that no reaction took place between it and the indole derivative.

With ethyl acetoacetate the reaction takes another turn, for only one molecule of 2-methylindole reacts with the molecule of ethyl acetoacetate. The resulting substance has the structure shown below:

$$N<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot CMe\cdot CH_2\cdot CO_2Et.$$

In these reactions with 2-methylindole the yields are quantitative, but when the parent substance indole is substituted for the methyl derivative the results are much less satisfactory, although the same types of end-products are produced with acetone, namely:

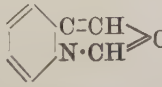
$$N<\begin{matrix}C_6H_4\\CH\end{matrix}>C<\begin{matrix}CMe_2\\CMe_2\end{matrix}>C<\begin{matrix}C_6H_4\\CH\end{matrix}>N \text{ and}$$

$$NH<\begin{matrix}C_6H_4\\CH\end{matrix}>C\cdot CMe_2\cdot C<\begin{matrix}C_6H_4\\CH\end{matrix}>NH.$$

Picolide and Pyrindole.

When α-picoline is treated with acetic anhydride it yields a compound having the composition $C_{12}H_{14}O_2N$, which has been termed picolide. This compound appears to be an *N*-acetyl derivative, as it shows no basic properties; it contains a ketonic oxygen atom, condenses with two molecules of aromatic aldehydes, and decomposes, on heating with hydrochloric acid, into a base having the composition C_8H_7N. This last substance was originally termed pyrrocoline, but it has been re-named pyrindole.[51]

Pyrindole is isomeric with indole, and its constitution has now been deduced to be:

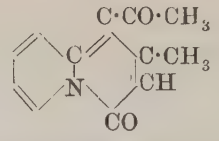


With regard to the constitution of picolide, the following evidence has been accumulated. Having no basic properties, it is probably an *N*-acetyl derivative. The second oxygen atom belongs to a carbonyl group, for picolide reacts with one molecule of phenylhydrazine, hydroxylamine, or semicarbazide; and when the Grignard reagent is employed, only one carbonyl group reacts with

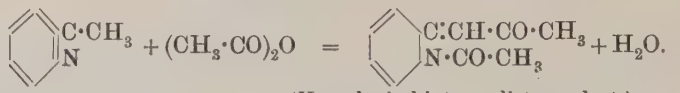
[51] M. Scholtz and W. Fraude, *Ber.*, 1913, **46**, 1069; *A.*, i, 514.

it, yielding a tertiary alcohol. Picolide is easily attacked by oxidising agents, and its condensation with two molecules of aromatic aldehydes tends to show that it has two free methyl groups so placed that they are sensitive to condensing reagents.

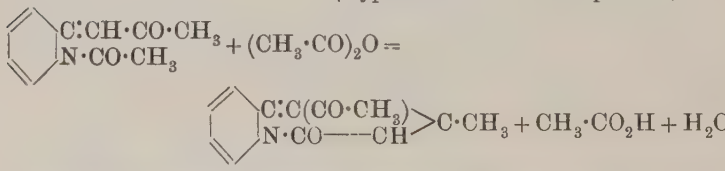
The only formula which appears to fit in with this evidence is the following:



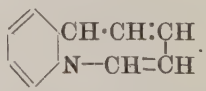
and on this assumption the formation of picolide would be represented by the following scheme:



(Hypothetical intermediate product.)

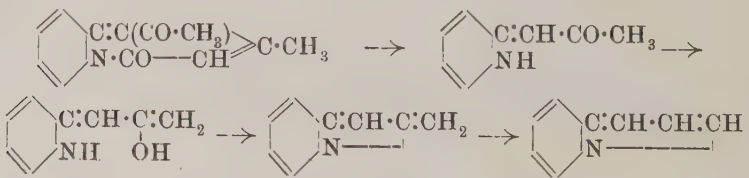


Picolide may be considered to be derived from a parent substance of the structure:

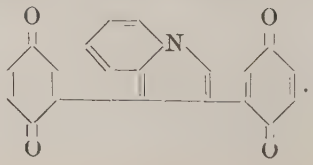


for which the name quinolizine is suggested.

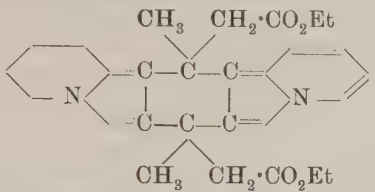
The conversion of picolide into pyrindole may be expressed as follows:



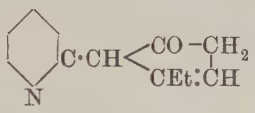
With regard to the reactions of pyrindole, the following appear to be the most important. Like the indole derivatives, it reacts with benzoquinone, yielding diquinonylpyrindole:



It condenses readily with ketones, two molecules of pyrindole reacting with one molecule of the ketone. Ethyl acetoacetate does not react as a normal ketone in this manner, but produces instead a substance which appears to have the structure shown below, and as can be seen by inspection, the two compounds have reacted in molecular proportions with each other:



It is not without interest to find that when propionic anhydride is substituted for acetic anhydride in the reaction of picolide formation, the results are totally different from the "normal" reaction. Propionic anhydride and picoline yield a substance having the composition $C_{12}H_{13}ON$, which, from an examination of its properties, appears to have the constitution:



so that it is in no way analogous to picolide.

Chlorophyll and Haemin.

The problems relating to the constitutions of these two substances may, at the present time, be regarded as among the most intricate which the field of organic chemistry contains. Not only are the reactions complicated in the extreme and the decomposition products obtained numerous and complex, but in addition the nomenclature is to a great extent different from the ordinary; thus anyone who desires to read up the subject is faced with difficulties greater than the ones which ordinarily attend the perusal of chemical papers. Further, the work is to a great extent dependent on the interpretations that can be placed upon the progress of certain reactions in which the reagents are so complex that it is very difficult to determine the composition of the substances, or even the number of carbon atoms which they actually contain, so that a fairly complete narrative of the work of the year would entail the description of reactions and their results in much greater detail than is possible within the compass of a Report such as the present. It seems well, therefore, on this occasion, to confine the Report to a brief sketch of barest outlines of the work, and to draw attention in particular to the suggestions put forward with respect to the structure of chlorophyll and hæmin.

Before entering into detail, it may be well to recall the meaning of certain terms which have come into use in this field. Chlorophyll, obtained from plants, was shown last year[52] to be a mixture of two components, chlorophyll-*a* and chlorophyll-*b*. These substances are derivatives of dicarboxylic acids in which the one carboxyl radicle is esterified with methyl alcohol, whilst the second carboxyl group is esterified with the alcohol phytol. If the phytol is hydrolysed away, the monomethyl ester remaining is termed a chlorophyllide. By the action of alkali on this chlorophyllide, hydrolysis takes place, the methyl group disappears, and a deep-seated rearrangement of the nucleus occurs, which results in the production of a new type of dicarboxylic acid. This new acid is termed a chlorophyllin. All the substances mentioned contain an atom of magnesium within the nucleus. This magnesium atom can be removed, and its place is then taken by two hydrogen atoms, with the result that a dicarboxylic acid called a porphorin is obtained from the phyllin class.

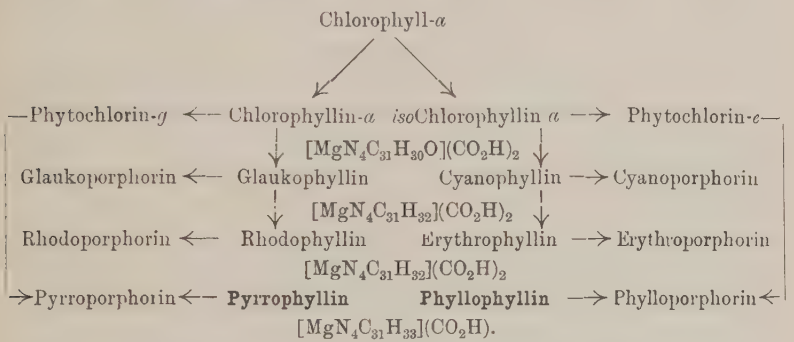
Now just as the chlorophyll derivatives contain an atom of magnesium, the hæmin derivatives from blood contain an atom of iron, and when this iron atom is removed, the reaction products are called porphorins as they resemble to some extent the corresponding chlorophyll compounds. From this apparent similarity between the chlorophyll and hæmin derivatives it was supposed until recently that there was a very close relationship between chlorophyll and hæmin, and it was generally assumed that hæmin was a kind of chlorophyll in which iron replaced the magnesium of true chlorophyll. This idea appears to have been incorrect in the light of the present year's work. In the succeeding sections an endeavour will be made to trace the steps in the reasoning which have led to this conclusion, and also to throw some light on the current ideas with regard to the constitutions of chlorophyll and hæmin.

*The Decomposition Products of Chlorophyll-*a *and Chlorophyll-*b.

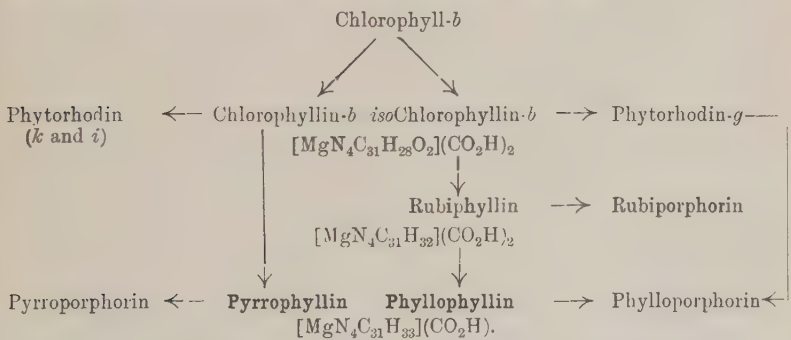
When ordinary chlorophyll is broken down, the final stages of the decomposition give rise to two isomeric substances, pyrrophyllin and phyllophyllin, which have the composition $MgN_4C_{31}H_{33}\cdot CO_2H$, and cannot be converted into each other by ordinary reactions. With the discovery that chlorophyll was not a single compound but a mixture of chlorophyll-*a* and chlorophyll-*b* came the idea that pyrrophyllin might be a decomposition product of the one variety

[52] *Ann. Report*, 1912, 165.

of chlorophyll, whilst phyllophyllin was the corresponding derivative of the second chlorophyll. Further investigation[53] has shown, however, that this view is incorrect, for when either chlorophyll-*a* or chlorophyll-*b* is subjected to degradation reactions, the end-products contain both pyrrophyllin and phyllophyllin. The difference between the two chlorophylls is confined to the substances themselves and the half-way stages of the degradation process; thus in the case of chlorophyll-*a* the decomposition takes place in accordance with the following scheme:



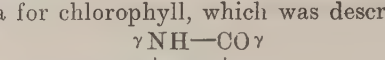
whilst with chlorophyll-*b* the reactions are expressed by:



From the differences in the above table it is clear that although probably the two chlorophylls both contain some grouping of atoms which gives rise to pyrrophyllin and phyllophyllin, yet their intermediate products of decomposition are not by any means identical. To explain the fact that a series of similar reactions when applied to the one chlorophyll yields results different from those obtained with the other chlorophyll, although the end-

[53] R. Willstätter, M. Fischer and L. Forsén, *Annalen*, 1913, **400**, 147; *A.*, i, 1215.

products are the same in each case, recourse may be had to the lactam formula for chlorophyll, which was described last year [54]:



Chlorophyll-*a*.

By the action of alkali on chlorophyll the colour of the component *a* is changed to yellow, whilst that of *b* becomes red, gradually coming back to green. It is assumed, to account for this, that a lactam ring is broken and a new lactam ring then formed, whilst in the meantime the complex union with the magnesium atom is ruptured. In the case of chlorophyll-*a* the process of lactam isomerism may take place in various ways; for example, in the change of chlorophyll-*a* into chlorophyllin, the lactam ring may be produced from the γ-carboxyl group and the δ-amino-radicle, yielding $\cdot\overset{\gamma}{C}O\cdot\overset{\delta}{N}H\cdot$, whereby the carboxyl groups α and β are left free in the molecule. In the change of chlorophyll-*a* into the isomeric lactam, *iso*chlorophyllin, the lactam ring may be formed between the α-carboxyl and the γ-amino-group, so that in this case two different carboxyl groups, γ and β, are set free. This illustrates the production of both chlorophyllin and *iso*chlorophyllin from the same component of chlorophyll, chlorophyll-*a*. On further treatment with alkali these two lactam groups are abolished, and the β-carboxyl radicle also disappears, with the result that a monocarboxyphyllin is formed in each case. These compounds are different from each other, which suggests that the carboxyl group left in the molecule occupies a different position in each of the two phyllins. This leads to the conclusion that the phyllin molecule cannot be symmetrical, and the experimental evidence available points also in this direction.

A further line of investigation in this field is not without interest. The table on p. 153 shows that when chlorophyllin-*a* is converted into glaukophyllin an oxygen atom disappears, and the suggestion has been made that a carbon atom disappears at the same time. This might be accounted for if it be assumed that a carbonyl group is eliminated from the ring, and that the remainder of the nucleus produces a pyrrole ring as shown below:

When the great complexity of the substances is borne in mind

[54] *Ann. Report*, 1912, 166.

it does not seem very strange that the question of whether the carbon atom remains in the molecule or not should be one which offers considerable analytical difficulties. and this example will suffice to remind the reader of the complexity of the problem and the tentative manner in which suggestions have to be made.

The Parent Substances of the Phyllins and Porphorins.

When chlorophyll is subjected to a series of degradation reactions the products are phyllins, which are carboxylic acids containing magnesium atoms in their molecules. Further degradation converts these into the corresponding porphorins, which are carboxylic acids with no magnesium atom in the molecule, the metallic atom being replaced by hydrogen atoms. Hæmin, when subjected to the same processes, also produces porphorins, but these are not identical with the chlorophyll decomposition products. The degradation products from hæmin and chlorophyll have this in common, however, that when they are subjected to energetic reactions, such as oxidation or reduction, the end-products of the reaction in either case are found to contain identical products, such as pyrrole derivatives. From this it appears probable that all the porphorins contain some common nucleus, and that the difference between them is due to the different manner in which other radicles are attached to this nucleus in the various compounds.

One possible difference of this kind might be sought in the different positions taken up by the carboxyl groups in the porphorin nucleus, and it seemed desirable to prepare the carboxyl-free substances from which the various porphorins are derived in order to find out whether the position of the carboxyl groups in the molecule was the governing factor in the question. This has now been accomplished,[55] and two compounds have been obtained, which appear to form the nuclei from which the porphorins and phyllins are derived. These substances have been named aetiophyllin and aetioporphorin, and their compositions are represented by $C_{31}H_{34}N_4Mg$ and $C_{31}H_{36}N_4$ respectively. The formulæ suggested for them are given on p. 157.

The three porphorins, phylloporphorin, pyrroporphorin, and rhodoporphorin, when heated with soda-lime, lose carbon dioxide and yield aetioporphorin, so that it becomes probable that the differences between the three substances are due to the various positions occupied by the carboxyl groups within their molecules. The reaction is such a violent one, however, that it seems possible that its results are not necessarily confined to the elimination of carbon dioxide; intramolecular change might occur as well, which would

[55] R. Willstätter and M. Fischer, *Annalen*, 1913, **400**, 182; *A.*, i, 1218.

perhaps account for the three substances yielding the same end-product.

From aetioporphorin it is possible to obtain aetiophyllin. The magnesium atom is introduced into the porphorin molecule by treating the latter in concentrated ethereal solution first with magnesium methyl iodide and subsequently with sodium dihydrogen phosphate. In the case of some other chlorophyll derivatives the introduction of magnesium can be carried out by heating the substance under pressure with methyl-alcoholic potassium hydroxide and magnesium oxide.[56]

The Probable Constitution of Haemin.

Hæmin, when treated with hydrobromic acid under certain conditions, produces hæmatoporphorin, from which the iron atom of hæmin is absent. If hæmin is treated with methyl-alcoholic potassium hydroxide in the presence of much pyridine, it yields the complex iron derivative of a substance called mesoporphorin, whilst hæmatoporphorin under the same conditions produces a compound termed hæmoporphorin.[57] When this is heated with soda-lime its carboxyl radicles are split off, and the end-product of the reaction is found to be identical with the aetioporphorin produced by the degradation of chlorophyll. Aetioporphorin having the composition $C_{31}H_{36}N_4$, it follows that its dicarboxylic derivative, hæmoporphorin, must correspond with the formula $C_{33}H_{36}O_4N_4$, and hæmoporphorin is therefore isomeric with the dibasic porphorins derived from chlorophyll. Further, since hæmoporphorin has been shown to be produced from hæmatoporphorin without any alteration in the carbon content of the latter substance, it follows that hæmatoporphorin also must have thirty-three atoms of carbon in its nucleus. Hitherto it has been assumed that there were thirty-four carbon atoms in the members of this series of compounds. It is now more probable that the following compositions should be ascribed to the hæmin group:

Hæmin, $C_{33}H_{32}O_4N_4FeCl$. Hæmatoporphorin, $C_{33}H_{38}O_6N_4$.
Mesoporphorin, $C_{33}H_{38}O_4N_4$.

Turning next to the question of the structure of these compounds, it is clear that the simplest derivative is aetioporphorin. Now the decomposition of the colouring matter of the blood results in various end-products, such as phyllopyrrole, hæmopyrrole, and kryptopyrrole, and from a consideration of the structures of these substances it appears most probable that the molecule of blood

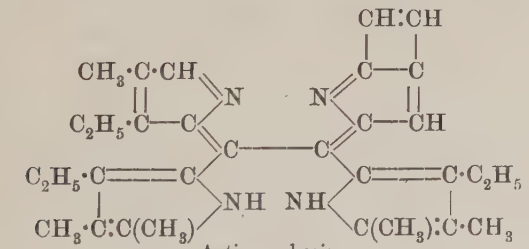
[56] R. Willstätter and L. Forsén, *Annalen*, 1913, **396**, 180; *A.*, i, 499.

[57] R. Willstätter and M. Fischer, *Zeitsch. physiol. Chem.*, 1913, **87**, 423; *A.*, i, 1251.

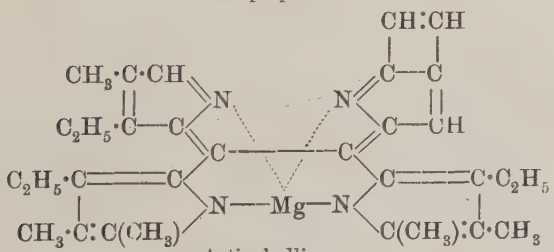
pigment contains no less than four different pyrrole nuclei, which are united together in a very peculiar manner; and it seems likely that these four nuclei are also to be found in the aetioporphorin molecule. Examination of the formula for aetioporphorin, $C_{37}H_{36}N_4$, shows that the number of hydrogen atoms is small when compared with the number of carbon atoms in the molecule, whence it may be deduced that the four pyrrole nuclei must be united to each other in such a way as to leave only a few positions free for hydrogen atoms to occupy.

W. Küster [58] has suggested a constitutional formula for hæmin which takes this point into consideration, but as his formula contains a sixteen-membered ring composed of four nitrogen and twelve carbon atoms, it will hardly recommend itself to the ordinary chemist unless no simpler structure can be suggested which will give equally satisfactory results. O. Piloty and E. Dormann [59] have also put forward a suggestion as to the structure of the hæmin molecule, but according to R. Willstätter and M. Fischer [60] this proposed formula will not account for the production of hæmatinic acid as a decomposition product of hæmin.

R. Willstätter and M. Fischer [61] have themselves brought forward a formula which they believe to cover most of the field. According to their view, aetioporphorin and aetiophyllin have the following structures:



Aetioporphorin.

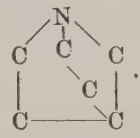


Aetiophyllin.

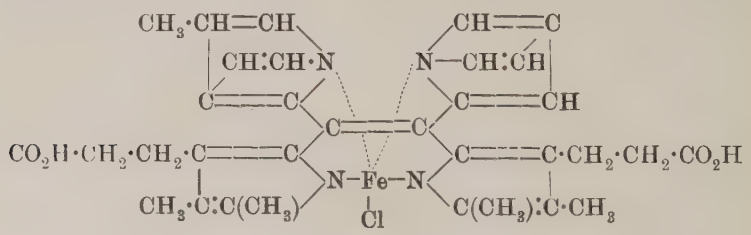
[58] *Zeitsch. physiol. Chem.*, 1912, **82**, 463; *A.*, i, 210.
[59] *Annalen*, 1912, **388**, 313; *A.*, 1912, i, 519.
[60] *Zeitsch. physiol. Chem.*, 1913, **87**, 423; *A.*, i, 1251.
[61] *Ibid.*

In these formulæ the small number of hydrogen atoms in the molecules is accounted for by the introduction of the vinyl group attached to a pyrrole ring. The position of this vinyl radicle has been arbitrarily chosen, and the position of the two methyl groups, as well as one or two other points, are merely provisionally allotted.

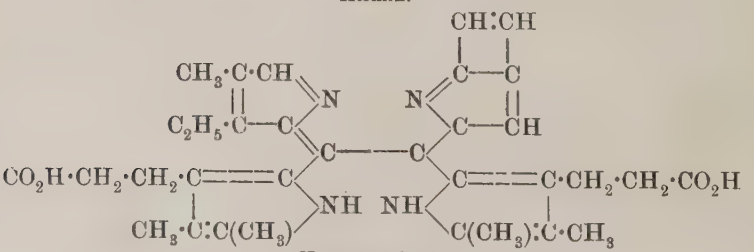
Assuming this formula for aetioporphorin, Willstätter and Fischer proceed to discuss the structure of hæmin itself. It appears from their work that in the decomposition of the hæmin molecule the elimination of the iron atom is not a direct process, but that, in the first place, the hæmin molecule takes up two molecules of halogen acid, and that thereafter it can be freed from the iron. Until the addition of halogen acid has occurred, it appears to be impossible to split off the iron atom from the rest of the complex. To account for this, it is assumed that the hæmin molecule contains a grouping similar to that which occurs in several of the alkaloids:



In this way, the following structures for hæmin and hæmoporphorin are arrived at:



Hæmin.



Hæmoporphorin.

Residual Affinity and Spatial Conjugation.

In last year's report[62] attention was drawn to the fact that in a six-membered dihetero-ring compound the nature of the atoms in the 1 : 4-positions had some influence on their reactivities. Further evidence on this point has come to light in a different field.[63] It has been shown that tetranitromethane is capable of producing colours when brought into the presence of compounds containing atoms which are capable of showing a rise in valency; thus, for example, an aliphatic sulphide contains a bivalent sulphur atom which is capable of becoming quadrivalent, and such sulphides when mixed with tetranitromethane yield colours. A group of six-membered cyclic substances containing all permutations of two atoms of sulphur, oxygen, and nitrogen in the 1 : 4-position to each other has been studied, and the following results have been observed. A single etheric oxygen yields with tetranitromethane a practically negligible tint (pentamethylene oxide), but when the more highly unsaturated sulphur and nitrogen atoms are employed, the substances containing them (pentamethylene sulphide and methylpiperidine) show marked tints. Two etheric oxygen atoms in the 1 : 4-position with regard to each other are able to reinforce each other so as to produce a colour, although a very pale one. When two sulphur or two nitrogen atoms are substituted for the oxygen ones, the tints are very markedly deepened; 1 : 4-dithian gives a lemon-yellow colour, whilst 1 : 4-dimethylpiperazine produces a brown tint. There appears to be a relation between the depth of the colour and the amount of residual affinity on the conjugated atoms. Finally, the conjugation of a strongly basic atom, nitrogen, with a less basic one, oxygen or sulphur, produces a golden-yellow colour, whereas the conjugation of two weakly basic atoms, oxygen and sulphur, yields the much less intense lemon-yellow tint. It appears that this reaction might form a rough gauge of the amount of residual affinity on various atoms. A comparison of cyclic substances with the corresponding open-chain compounds tends to show that the opening of the chain makes no very marked difference in the tints produced.

A continuation of this investigation with the spectrograph[64] has shown that in all cases an absorption band is present which has its head at oscillation frequency 2800—2900, no matter whether the compound treated with tetranitromethane be an amino-compound,

[62] *Ann. Report*, 1912, 163.

[63] H. T. Clarke, A. K. Macbeth, and A. W. Stewart, *P.*, 1913, **29**, 161.

[64] E. M. Harper and A. K. Macbeth, *ibid.*, 304 ; see also C. K. Tinkler, *ibid.*, 278.

a sulphide, or an ethylene derivative, so that the production of the band is evidently due to some perfectly general process, and is not specially concerned with the particular atom involved. It has also been shown that the penetration of the band in most cases increases if the solutions are kept, and in this way it is possible to estimate the relative speeds with which two compounds react with tetranitromethane. The nature of the solvent used is also a factor in the problem. It appears not improbable that when this method is further developed it may furnish a very simple means of estimating the residual affinity of various compounds, and by a further extension it may allow of the study of the residual affinity of the various solvents which can be utilised.

Optical Activity in the Heterocyclic Compounds.

One or two points of interest have arisen during the year in this section of the subject. Previous investigations have shown the possibility of isolating optically active forms of compounds containing quadrivalent sulphur or selenium atoms, and an attempt has now been made to resolve an oxonium derivative into its antipodic isomerides.[65] The substance chosen as a starting material was 2-phenyl-6-methyl-4-pyrone, which has the advantage that its hydrochloride is not hydrolysed in aqueous solution. From the hydrochloride the *d*-bromocamphorsulphonate was prepared in the usual manner. It has the structure shown below, and the quadrivalent oxygen atom is an asymmetric one:

$$CO\begin{<}CH{=}CPh\\CH{:}CMe\end{>}O\begin{<}H\\SO_3\cdot C_{10}H_{14}OBr\end{>}\cdot$$

The resolution has not yet been carried out owing to lack of sufficient material, but the results obtained up to the present point to the probability of success when experiments can be carried out with larger quantities.

A case in which stereoisomerism gives rise to a very large number of isomeric compounds has been discovered among the tetrahydroquinaldine derivatives.[66] When *d*- and *l*-tetrahydroquinaldine are condensed with *d*- and *l*-oxymethylenecamphor, four simple optically active tetrahydroquinaldinomethylenecamphors are produced, any two of which can combine together with the formation of a stable double compound; thus the complete series of derivatives includes the four simple active, two fully racemic, and four partly racemic compounds, ten in all.

[65] S. I. Levy, E. J. Holmyard, and S. Ruhemann, *P.*, 1913, **29**, 159.
[66] W. J. Pope and J. Read, *T.*, 1913, **103**, 1515.

The relation between optical activity and enantiomorphism of molecular structure has been very much in the forefront of stereochemical theory during the past few years, and the classic case of the diketodialkylpiperazines[67] should perhaps be dealt with in this section of the Reports. As the paper in which it is treated, however, bears on the wider field of crystalline structure it seems best to let the whole subject be dealt with under one head, and the reader is therefore referred to the Report on Mineralogical Chemistry in this volume.

A. W. Stewart.

[67] T. V. Barker and J. E. Marsh, *T.*, 1913, **103**, 837.

ANALYTICAL CHEMISTRY.

This report follows the same general plan as that of last year, but fewer papers have been selected for notice, and these have been referred to at somewhat greater length. Consideration of the few papers dealing with water analysis is deferred until another year, when there may be more to record, but the physiological section, omitted last year, has been restored. The determination of water in various materials has received an unusual amount of attention recently, and this subject has been selected for special notice.

General.

A new method has been found for the determination of hydroxyl-ion concentration, comparable to the method for determining the concentration of hydrogen ions, which depends on the velocity of hydrolysis of ethyl diazoacetate.[1] It was announced last year that it appeared probable that the decomposition of nitrosotriacetonamine by alkalis into phorone and nitrogen would afford a means for the quantitative determination of hydroxyl ions,[2] and further results which have been obtained leave no doubt that the view expressed in the first communication is correct. The velocity constants have been established in presence of aqueous solutions of sodium, potassium, and barium hydroxides, and found to be proportional, not to the concentration of the bases themselves, but to the concentration of hydroxyl ions as deduced from conductivity measurements. The importance of the method lies in the fact that the effect of neutral salts in ordinary concentration is negligible. In any individual experiment the values of the velocity constant agree to within 1—2 per cent., and the results are reproducible to within 2—3 per cent. The method is consequently available with this degree of accuracy for the estimation of the concentration of hydroxyl ions up to $0{\cdot}05N$, and the general formula may be expressed as follows:

$$\text{Concentration of } OH' = K_{tz}/R,$$

[1] G. Bredig and W. Fraenkel, *Zeitsch. Elektrochem.*, 1905, **11**, 525; *A.*, 1905, ii, 692.

[2] D. A. Clibbens and F. Francis, *T.*, 1912, **101**, 2358.

where $R = 1{\cdot}96 \times 2{\cdot}20^{\frac{t^\circ - 30}{10}}$, and K_{t° is the observed constant at the temperature t°. Between concentrations of $0{\cdot}05N$ and $0{\cdot}3N$, the unimolecular constants "drift," and the method is consequently inapplicable within these limits. The drift ceases, however, at the latter concentration, and the method is once more applicable, but with diminishing accuracy, up to about $1{\cdot}4N$, beyond which point the velocity constants change so slightly with large increases in the concentration of hydroxyl ions that a limit is set to the range of the method as a means of measuring such concentrations accurately.[3]

It is nearly forty years since Lecoq de Boisbaudran described his method for producing arc spectra. Some of the advantages of the method were immediately apparent, but the principle has found less extended application than would have been the case had any simple device for producing the arc been readily obtainable. One may search in vain for such device in any catalogue, and the authors of a recent paper are probably right in stating that an apparatus devised by them represents the first attempt to bring the method within reach of everyone. They establish an arc between the liquid to be examined and an iridium needle, taking current from an ordinary lighting circuit at 100—200 volts through an adjustable resistance. The length of the arc is adjustable by means of a micrometer screw, and the whole apparatus is mounted on a stand facilitating vertical and horizontal adjustment of the position of the arc relative to the spectrometer. No air lines appear, and the iridium electrode gives rise only to lines which are negligibly faint. The hydrogen line, $656\mu\mu$, appears as a brilliant line, the line $486\mu\mu$ as a bright one. With this apparatus, not only may magnesium be detected in concentrations of 0·1 mg. per c.c. by means of the three brilliant lines 516·8 to $518{\cdot}4\mu\mu$, but calcium, strontium, and particularly barium, can be detected in far lower concentrations than is the case when a Beckmann burner or other means for producing a flame spectrum is employed. In the case of barium, the concentration necessary to ensure detection is reduced from 14 mg. to 0·006 mg. per c.c., and in that of calcium from 0·2 mg. to 0·002 mg.[4]

Advance in the technique of handling minute quantities of solids and liquids in a quantitative manner continues to depend mainly on a single worker. During the year improvements have been introduced which greatly increase the accuracy of results depending on the handling of minute precipitates. Precipitation is now con-

[3] F. Francis and F. H. Geake, *T.*, 1913, **103**, 1722.

[4] E. H. Riesenfeld and G. Pfützer, *Ber.*, 1913, **46**, 3140; *A.*, ii, 1074.

ducted in small platinum dishes, in which the substance to be analysed is weighed, dissolved, and precipitated. After filtration of the liquid through the micro-filter previously described,[5] the dish is dried and re-weighed, together with the dried filter, so that no part of the precipitate which may adhere to the dish escapes weighing. These dishes need to be 20 mm. or more in diameter, and must be very light in proportion to their size. Thin foil is seldom free from pinholes, and it is found that dishes of the minimum weight consistent with freedom from pinholes are best made from two or three disks of very thin foil welded together. Directions are given for cutting and welding the disks and shaping them into basins. Quantities as small as 1 mg. can now be manipulated with an error not exceeding a few tenths of 1 per cent. It is pointed out that, now that such accuracy as this is attainable, the use of micro-methods should not be restricted to cases where very small quantities of substance are available. By their means many determinations can be made more quickly than is possible when working on large quantities.[6] From the same laboratory a qualitative test for bismuth and manganese has been announced. It is mentioned here rather than in a later section of this report, as its interest lies less in the particular results so far attained than in the nature of the reaction and its extraordinary sensitiveness. When a drop of a dilute solution of a salt of bismuth or manganese is allowed to fall on a piece of pure chalk or gypsum, and this is heated in a hydrogen flame, a brilliant blue (Bi) or bluish-green (Mn) luminescence is produced. One ten-millionth of a milligram of bismuth, or one millionth of a milligram of manganese will give the reaction.[7]

The determination of water has formed the subject of a number of papers during the past three years. Some of these papers are important as recording the results of a critical investigation of the methods available for the determination of water in a particular material, but, because indexed under the name of that material, will have few readers. Nearly every recent paper on the subject, however, has this general interest, that it emphasises the fact that the exact determination of water, whether in minerals or in organic materials, is one of the most difficult problems presented to the analyst, and no problem presents itself more often to workers in every branch of analytical chemistry. In simple cases, the problem is essentially identical with that of obtaining a substance truly dry, a problem so difficult that the Faraday lecturer of 1911 expressed the view that failure to solve it had been one of the two most fertile

[5] *Ann Report*, 1912, 196.

[6] J. Donau, *Monatsh.*, 1913, **34**, 553; *A.*, ii, 424.

[7] *Ibid.*, 949; *A.*, ii, 743.

sources of error in the determination of atomic weights.[8] More often, however, the determination of water is complicated by the fact that it cannot be expelled from the material with which it is associated without bringing about other changes in the material besides loss of water.

For the determination of water in silicate minerals and rocks, the the well-known method of Penfield may give results far below the truth, unless the tube be wrapped round with platinum as Penfield directed, and the temperature raised to such a point that the platinum adheres to the glass. The fact that it requires no apparatus beyond what is to be found in every laboratory will, however, cause Penfield's method to be retained for service with the large number of minerals and rocks which yield the whole of their water at moderate temperatures. The Ludwig-Sipöcz method, consisting in heating the powdered rock with fusion mixture in a current of dry air, and collecting and weighing the water, has been improved by the use of a silica combustion tube with ground joints, and by the substitution of sodium carbonate for a mixture of sodium and potassium carbonates. All silicate rocks yield to this method, which has the added advantage that the residue is immediately available for the determination of silica, alumina, etc. If the determination of water is the only object, this may be attained by heating the material alone in a silica tube, provided an electric furnace capable of giving a temperature up to 1250° is available. Given the necessary apparatus, this is the best general method, provided the water be collected and weighed, since it is applicable to all rocks except such as contain fluorides. The authors of this work publish results obtained with a large number of named minerals and rocks, using the above methods and others. This is useful as showing how far the elegant method of Penfield may still be retained for exact work, and also as showing the errors attaching to all methods which determine "water" by difference.[9]

Since the publication in 1895 of a Report on Coal Analysis by a Committee of the American Chemical Society, much work has been carried out with the object of improving methods for the determination of moisture in coal, and this work is of general interest, as the problem does not differ in essentials from that of determining moisture in many organic materials which may lose other volatile constituents or absorb oxygen at temperatures at or below 100°. The Seventh International Congress of Applied Chemistry appointed a Committee to investigate and report on methods for the deter-

[8] T. W. Richards, *T.*, 1911, **99**, 1201.

[9] M. Dittrich and W. Eitel, *Zeitsch. anorg. Chem.*, 1912, **75**, 373; *A.*, 1912, ii, 804; *ibid.*, **77**, 365; M. Dittrich, *ibid.*, **78**, 191; *A.*, 1912, ii, 1207.

mination of moisture in coal, and the more important conclusions of this Committee have since been given wider publicity by being incorporated in a paper with the general title, "The determination of moisture." The reading of this paper was followed by that of two others dealing with the same general subject, with special reference to foodstuffs. For the determination of moisture in organic materials containing no other volatile constituents, drying in a vacuum at the ordinary temperature has some obvious advantages, but since the water on the surface of a fine powder has a lower effective vapour pressure than water *per se*, the rate of drying in such a vacuum as can be obtained by the use of a water pump is very slow. Even with a vacuum of 1 mm., twenty-four hours or more is necessary. The International Committee suggests weighings after one, three, and six days. Such periods as this are probably unnecessary, and, since a two-cylinder Fleuss pump will give a vacuum of 0·01 mm., or less, it is possible that the use of such a pump, together with an arrangement for circulating the sulphuric acid in the desiccator, might reduce the necessary period to one or two hours, an important consideration in technical work. It is to be noted that, in work of this kind, phosphoric oxide is not nearly so trustworthy a desiccating agent as concentrated sulphuric acid.

When the material to be examined contains other volatile constituents besides water, a direct method must be used. Heating in a current of dry air, with collection and weighing of the moisture carried forward by the air current, is not admissible in the case of coal or of many other naturally occurring organic materials, because these materials, although not affected by mere heating to 100° or a little higher for prolonged periods, suffer change when exposed to air at 100° or less, water being one of the products. Even a small percentage of oxygen in the gas used may lead to serious error, and many materials absorb carbon dioxide. Heating in a current of pure, dry nitrogen, with collection and weighing of the water evolved, is therefore indicated as the only direct method likely to prove of wide application. When skilfully conducted, it leaves little to be desired in point of accuracy, but requires for its accurate conduct more knowledge and care than is commonly supposed. Notwithstanding their undoubted merits, neither the vacuum nor the direct method can be expected to come into general use for technical purposes, which require, however, some means for determining moisture in organic materials with a close approximation to accuracy.

Drying in an ordinary oven at about 100° will no doubt continue to be the most usual method of determining moisture in

organic materials other than those containing appreciable proportions of volatile substances other than water. Old as the method is, it has quite recently been found possible to effect a notable improvement in the results which can be obtained by its means. Of its inherent sources of error, that due to absorption of oxygen is now known to be the most important. That this is so in the case of coal has long been known, but it has now been established as the chief source of error in drying the most widely variable organic materials of natural origin. As the degree of oxidation is a function of the time of exposure to air at a high temperature, the analyst's aim must be to expel the moisture as quickly as possible. Renewal of the air in the oven, as frequently as is possible without material reduction of temperature, is one means of advancing this aim. Another lies in drying at temperatures slightly above instead of below 100°. Experience has now accumulated to show that a very wide range of organic materials resemble coal in not being appreciably more affected by exposure to air at 105—110° than by exposure to air at 99°, and since water is far more quickly eliminated at the higher temperature, the use of an oven heated to this temperature by toluene vapour or other means should become more general.[10] Reference may fitly be given to one of the ovens recently described,[11] which seems particularly well adapted for drying organic materials. It ensures a uniform temperature of the walls of the oven, and, by having the wall area large in proportion to the cubic capacity, a fairly uniform temperature of the interior. An adequate supply of pre-heated air is also secured by chimney draught.

The determination of water in petroleum and its products is a problem of comparatively narrow interest, but a recent review of ten methods, all of which have found more or less extended use for the purpose, together with the reasons which lead the authors to prefer that depending on the volume of hydrogen evolved when the sample is treated with sodium, may perhaps be found useful by chemists called on to discover the most accurate means of determining water in some other organic liquids.[12]

Only a few of the more recent papers on the determination of water are cited here, but these papers between them almost cover the ground, and each gives references to earlier work.

[10] G. N. Huntly and J. H. Coste, *J. Soc. Chem. Ind.*, 1913, **32**, 62; F. H. Campbell, *ibid.*, 67; W. P. Skertchly, *ibid.*, 70; *A.*, ii, 237, 238.

[11] J. H. Coste, *ibid.*, 1912, **31**, 471; *A.*, 1912, ii, 678.

[12] I. C. Allen and W. A. Jacobs, *Eighth Int. Cong. App. Chem.*, 1912, X, 17.

Gas Analysis.

In 1910 Erdmann and Stoltzenberg showed that certain simple gas mixtures could be analysed with great exactness by application of the principle of fractional condensation by liquid air, etc. The particular gas mixtures investigated by these authors can be readily analysed by ordinary methods, but, in calling attention to their work, the reporter of 1910 suggested that the principle of their method might find useful application in supplementing the ordinary methods of gas analysis in difficult cases.[13] Such an application is one recently described for the analysis of mixtures of hydrogen, methane, ethane, propane, and β-methylpropane. The mixture is subjected to the temperature of liquid air, and the hydrogen and methane are pumped off and then separately estimated in the usual manner.[14] The mixture is now allowed to attain a temperature of −127° and maintained at this temperature by suitable means, and the pump is once more set in operation. The whole of the ethane with some propane is thus removed, and the mixture analysed eudiometrically, as is the residual mixture of propane and β-methylpropane after being allowed to attain the gaseous state.[15]

The use of bromine or of fuming sulphuric acid to absorb olefines is attended with great inconvenience, and a recent announcement, that ordinary concentrated sulphuric acid containing 1 per cent. of vanadium pentoxide serves equally well, will no doubt lead to this elegant modification being tested in many laboratories. Absorption is rapid, the absorptive capacity of the reagent high, and so far as is known no gas which resists fuming sulphuric acid is attacked by the new reagent. A new reagent for absorbing acetylene and its homologues has also been described. It consists of a solution of mercuric and potassium iodides containing a trace of alkali hydroxide, has an absorptive capacity of 20, and olefines are no more soluble in it than in water.[16]

A direct method, by which nitrogen in gas mixtures can be estimated with an error not exceeding 0·3 c.c., is worthy of notice, even although the somewhat elaborate apparatus it requires will probably restrict its use to cases where a direct estimation is specially desirable. It depends on the fixation of the nitrogen as calcium cyanamide, which is then submitted to Kjeldahl's process. Like earlier investigators, its author finds that calcium cyanamide needs rather special treatment in the early stages of the Kjeldahl process, but, given that treatment, it does yield the whole of its

[13] *Ann. Report*, 1910, 160.

[14] P. Lebeau and A. Damiens, *Compt. rend.*, 1913, **156**, 144, 325; *A.*, ii, 253.

[15] P. Lebeau and A. Damiens, *Bull. Soc. chim.*, 1913, [iv], **13**, 366.

[16] P Lebeau and A. Damiens, *Compt. rend.*, 1913, **156**, 557; *A.*, ii, 349.

nitrogen as ammonia.[17] The apparatus required for the quantitative fixation of nitrogen as calcium cyanamide, although consisting of many parts and requiring time to assemble, could be improvised from existing apparatus in almost any laboratory.[18]

Inorganic Analysis.

Qualitative.—A very delicate test for bromine depends on the violet-blue colour which it imparts to filter paper which has been dipped in Schiff's aldehyde reagent and then dried between other pieces of filter paper. The colour is readily distinguished from that given by aldehydes, is not given or influenced by the simultaneous presence of iodine or chlorine, and will detect 0·01 mg. of potassium bromide when this is warmed with chromic acid solution and a test paper exposed to the escaping vapours. A fraction of a milligram suffices for the detection, in a similar manner, of bromine in an organic substance, and by operating on increasing quantities of commercial iodides or chlorides until the reaction is given, the order of magnitude of their bromine content can be determined.[19] The procedure is simpler than that recommended by Denigès, who has since devised a very similar test.[20]

Although less sensitive than the diphenylamine reaction, a new test for the detection of nitrate in presence of nitrite is deserving of reference, because it is available in presence of ferric salts. It depends on the blue colour which traces of nitric acid impart to a solution of quadrivalent iridium in concentrated sulphuric acid, and will detect 0·1 mg. of nitrate in the presence of 1 gram of nitrite.[21]

Reynoso's method for the separation of phosphoric acid in the course of qualitative analysis, by boiling the nitric acid solution with tin, requires considerable experience for its successful conduct. Since it was recognised that the method depended on the adsorption of phosphoric acid by metastannic acid, however, there was reason to hope that some modification of it might be evolved which could be applied with confidence by any chemist in any ordinary circumstances.[22] Such a modification has now been described, the method consisting in boiling the nitric acid solution with a considerable quantity of metastannic acid gel, prepared in a particular manner. Less than 0·1 per cent. of the phosphoric acid present finds its

[17] *Ann. Report*, 1911, 178.

[18] B. Natus, *Zeitsch. anal. Chem.*, 1913, **52**, 265; *A.*, ii, 527.

[19] I. Guareschi, *Atti R. Accad. Sci. Torino*, 1912, **47**, 696, 988; *A.*, 1912, ii, 989; *ibid.*, 1913, **48**, 4; *Zeitsch. anal. Chem.*, 1913, **52**, 607; *A.*, ii, 333.

[20] G. Denigès, *Compt. rend.*, 1912, **155**, 721; *A.*, 1912, ii, 1208.

[21] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1772; *Chem. Zeit.*, 1913, **37**, 157; *A.*, ii, 149.

[22] W. Mecklenburg, *Zeitsch. anorg. Chem.*, 1912, **74**, 215.

way into the filtrate, and no tin passes into solution unless chlorides are present. Iron, titanium, and zirconium are wholly retained by the gel, portions of which may be tested directly for the presence of iron and titanium.[23]

To be of real service in the analysis of zinc ores, a test for cadmium must be roughly quantitative. The test devised some years ago by Biewend, depending on reduction in a narrow glass tube with subsequent conversion of the sublimate into sulphide, makes it possible to estimate 0·01 per cent. of cadmium with no greater error than attaches to an estimation of arsenic by the Marsh-Berzelius method, which this test somewhat resembles.[24] Biewend's test, however, requires some time, and in many cases all that is required is to know whether there is less than some assigned amount of cadmium, such as 0·1 per cent., present. A test has now been devised which can be blunted to this or any desired extent, by varying the amount of material taken, which only requires a few minutes to carry out, and serves for the approximate estimation of heavier traces than those it is desired to detect. It depends on the production of a sublimate of cadmium oxide on porcelain.[25]

A paper on the qualitative analysis of the zinc group is a good example of the work being done by American chemists to put qualitative analysis on a better basis. Other people may write text-books or devise supersensitive tests, but Americans want methods of which it can be said with certainty that they will detect 1 mg. in a sample of a certain size and fail to detect some smaller assigned amount, and, so far as we possess such methods, we owe them largely to American workers. It is not uncommon to hear American methods spoken of with impatience, because such methods involve the frequent use of measured quantities of reagents, but this paper abundantly justifies the rough measurements required, and shows that such measurements are but part of the American method, which often requires, as in this case, the invention of entirely new methods of separation. A scheme of analysis which will detect with certainty 0·5 mg. of zinc, manganese, nickel, or cobalt in presence of large quantities of any of the others will prove of considerable practical value to many.[26]

Quantitative.—As the decomposition of silicates is often the first step in quantitative analysis, the first reference under this heading may fitly be to a paper which deals with the use of barium carbonate for decomposing silicates. One advantage of the method

[23] W. Mecklenburg, *Zeitsch. anal. Chem.*, 1913, **52**, 293; *A.*, ii, 529.

[24] R. Biewend, *Berg.-Huttenm. Zeit.*, 1902, **61**, 401; *A.*, 1903, ii, 105.

[25] F. C. Breyer, *Eighth Inter. Cong. App. Chem.*, 1912, xxv, 1; *A.*, ii, 793.

[26] R. E. Lee, R. H. Uhlinger, and F. O. Amon, *J. Amer. Chem. Soc.*, 1913, **35**, 566; *A.*, ii, 530.

is the ease with which barium can subsequently be eliminated; another, the fact that a crucible weighing only 4 grams suffices for the decomposition of 1 gram of felspar and the like. A temperature of 1350° is required, but this is readily attained by means of the electric furnaces now procurable, and the author has designed a special furnace by means of which a small crucible, such as suffices for this method, may be raised to the requisite temperature by a blowpipe flame.[27]

It is found that hydrogen peroxide can be determined iodometrically if molybdic acid is employed as catalyst. Molybdic acid is one hundred times as effective as iron salts, and has the further advantage that it appears to have no accelerating effect on the reaction between potassium iodide and atmospheric oxygen. By an extension of the method, hydrogen peroxide and ozone can be estimated in presence of each other.[28]

Selenic acid is capable of reacting with bromides and chlorides, with liberation of the halogen and formation of selenious acid, but the reaction in either case is a reversible one. Researches directed to determining the conditions under which the reaction with bromide is approximately quantitative, and that with chloride almost wholly inhibited, have been so far successful that a new method for the estimation of bromide in presence of chloride has been based on the results obtained.[29] As selenic acid obtained by the usual methods is apt to retain impurities which interfere with its use for the above purpose, reference may be made to a method by which it may readily be obtained of a satisfactory degree of purity.[30]

An entirely new and very accurate method for the estimation of fluorine has been described. It depends on the fact that, when sufficient ferric chloride is added to a neutral solution of an alkali fluoride the whole of the fluorine separates as a white, insoluble fluoride of the type Na_3FeF_6. The end-point of a simple titration with thiocyanate as indicator is not easily seen, but when the slight solubility of the precipitate is still further repressed by a large addition of chloride, and some ether and alcohol are also added, the characteristic red colour makes its appearance in the ethereal layer with such sharpness that the method is nearly as accurate as a volumetric method can be. In combination with acidimetric methods it greatly simplifies the analysis of commercial

[27] W. Hempel, *Zeitsch. anal. Chem.*, 1913, **52**, 86; *A.*, ii, 244.

[28] V. Rothmund and A. Burgstaller, *Monatsh.*, 1913, **34**, 693; *A*, ii, 524.

[29] F. A. Gooch and P. L. Blumenthal, *Zeitsch. anorg. Chem.*, 1913, **80**, 161; *A.*, ii, 148.

[30] P. L. Blumenthal, *ibid.*, 246; *A.*, ii, 148.

sodium fluoride, which usually contains sodium hydrogen fluoride and sodium silicofluoride.[31]

When a nitrite is added to an acid solution of thiocarbamide the reaction may proceed in two directions, depending on the strength of the acid; thus in presence of acetic acid the reaction takes place mainly in accordance with the equation:

$$CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O,$$

whilst in the presence of hydrochloric acid the reaction

$$2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O$$

predominates. Since the volume of gas produced by a definite weight of nitrous acid is the same whichever course the reaction takes, the fact that neither reaction can be wholly repressed is of no importance so far as the gasometric determination of nitrites is concerned. A gasometric method based on these observations gives exact results with silver nitrite, is shown to be accurate in presence of ten times as much nitrate as nitrite, and, so far as it gives results in disagreement with those obtained by the carbamide method, as it does with certain commercial preparations, is probably to be preferred to that method.[32]

Feld's original method for the estimation of polythionate in presence of thiosulphate and free sulphurous acid gives satisfactory results when the amount of sulphur dioxide in the solution is small,[33] but when much sulphur dioxide is present a large part of it may escape before oxidation is complete. A modification of the method has now been described which is free from this objection. It depends on the fixation of sulphur dioxide as manganous thiosulphate by treatment with excess of manganous sulphide; on subsequent treatment with mercuric chloride the manganous thiosulphate liberates hydrochloric acid[34] in accordance with the now well-known equation of Feld, on which his method for the estimation of thiosulphate is based. This method also has come under review during the year, and it is pointed out that, in presence of excess of mercuric chloride, a solution of a bisulphite, previously neutral to methyl-orange, reacts acid towards that indicator, and continues to do so until sufficient alkali is added to convert the whole of the bisulphite into normal sulphite. Consequently, Feld's method for the estimation of thiosulphate must fail in presence of sulphites or bisulphites. A simple modification of the method, however, meets the case, and the above observations have been made the basis of a method for the analysis of mixtures of normal

[31] A. Greeff, *Ber.*, 1913, **46**, 2511; *A.*, ii, 975.
[32] Miss M. E. Coade and E. A. Werner, *T.*, 1913, **103**, 1039.
[33] W. Feld, *Zeitsch. angew. Chem.*, 1911, **24**, 290; *A.*, 1911, ii, 289.
[34] W. Feld, *ibid.*, 1913, **26**, 286; *A.*, ii, 617.

and acid sulphite which is far more satisfactory than methods depending on the use of phenolphthalein.[35] Another method for the analysis of mixtures of thiosulphate with normal and acid sulphite depends on the use of hydrogen peroxide in place of Feld's mercuric chloride.[36] The methods available for the estimation of hyposulphites have been subjected to a critical review, the limits of accuracy of methods depending on the reduction of mercuric chloride—useful for technical purposes—have been established, and two other methods are shown to be exact, except in presence of large quantities of bisulphite, when the error may reach 0·3 per cent.[37]

Two papers on the estimation of silver deserve a word. One of them calls attention to the fact that Volhard's method gives results that may be 0·4 per cent. too high, due to adsorption of ammonium thiocyanate by silver thiocyanate, and shows how the error due to this cause may be reduced to negligible proportions.[38] The other paper, issuing from the United States Mint, shows that, even under the favourable conditions of a mint laboratory, two assayers, working on identical samples of standard silver and making four estimations each by Gay Lussac's method, may differ as much as 1 fine in their reports. Nevertheless, the method is preferred to fire assay for mint work. It is useless for a person who uses it only occasionally to expect to attain high accuracy with it without spending more time on a determination than is warranted in a busy commercial laboratory.[39]

Although there is a choice of good methods for the estimation of copper, the empirical method of Guess must have been found specially convenient in certain circumstances, or it would not have found its way into textbooks such as Low's "Technical Methods of Ore Analysis," which ignores redundant methods. The method depends on the precipitation of copper as thiocyanate, which is decomposed on the filter by means of sodium hydroxide, and the resulting solution of sodium thiocyanate is acidified and titrated with permanganate. Under the conditions prescribed by Guess, the reaction between thiocyanate and permanganate does not proceed quantitatively, and it has been usual for each operator to determine and apply an empirical factor.[40] Although the original method gave satisfactory results in experienced hands, a recent modification, which ensures a quantitative reaction between thiocyanate and

[35] E. Bosshard and W. Grob, *Chem. Zeit.*, 1913, **37**, 465; *A.*, ii, 525.
[36] A. A. Besson, *ibid.*, 926; *A.*, ii, 874.
[37] E. Bosshard and W. Grob, *ibid.*, 423, 437; *A.*, ii, 428.
[38] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 66; *A.*, ii, 340.
[39] F. P. Dewey, *J. Ind. Eng. Chem.*, 1913, **5**, 209; *A.*, ii, 340.
[40] H. Grossmann and L. Hölter, *Chem. Zeit.*, 1909, **33**, 348; *A.*, 1909, ii, 449.

permanganate, is more likely to be of general use.[41] A recent paper[42] on the estimation of cadmium is valuable, not only because three good methods are described in detail, but because the special circumstances in which one or other is to be preferred are plainly indicated. The choice of method is generally determined by the amount of cadmium present, and by the ratio of this amount to that of zinc.

The titration of antimony by permanganate in sulphuric solution free from hydrochloric acid is the only novel feature in a recent scheme for the analysis of white metals, but the scheme as a whole is deserving of attention because of the speed with which an analysis can be completed with sufficient accuracy for many purposes.[43] Accurate and rapid methods are now available for the determination of tin in ores and alloys, but a method depending on titration with potassium bromate may be referred to. Although not published before, the method has been in use for some time in silk-works, where the fact that it is available in the presence of phosphates is an advantage.[44] The separation of antimony from tin is referred to under "Electrochemical Analysis."

It has been shown that all the methods generally recommended for the estimation of free acid or free base in commercial aluminium sulphate give inaccurate results, the only method described in Lunge's "Technical Methods" actually discovering 0·25 per cent. free acid in each of a number of samples ranging from neutral to strongly basic. An exact method has now been devised, depending on the fact that neutral salts of aluminium are precipitated on warming with potassium ferrocyanide.[45]

A recent method for the estimation of zinc involves the application to an analytical problem of the mutual precipitation of two colloids. The particular colloid selected to assist the precipitation of zinc sulphide is sulphur, sodium hydrogen sulphite being added to the chloroacetic acid solution of zinc, through which hydrogen sulphide is then passed. The paper includes some useful information on the ignition of zinc sulphide precipitates.[46]

Attention may be called to a careful study of the sources of error in the assay of platinum, which is followed by the description of a method stated to give results correct to 1 part in 1000.[47]

[41] D. J. Demorest, *J. Ind. Eng. Chem.*, 1913, **5**, 215; *A.*, ii, 341.

[42] W. D. Treadwell and K. S. Guiterman, *Zeitsch. anal. Chem.*, 1913, **52**, 459; *A.*, ii, 728.

[43] D. J. Demorest, *J. Ind. Eng. Chem.*, 1913, **5**, 842; *A.*, ii, 982.

[44] F. Fichter and E. Müller, *Chem. Zeit.*, 1913, **37**, 309; *A.*, ii, 347.

[45] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 57; *Chem. Zeit.*, 1913, **37**, 805; *A.*, ii, 1078.

[46] K. Bornemann, *Zeitsch. anorg. Chem.*, 1913, **82**, 216; *A.*, ii, 727.

[47] L. S. Rainer, *Oesterr. Zeitsch. Berg.-u. Hüttenw.*, 1913, **61**, 141, 155.

Palladium may be separated from any of the other platinum metals by precipitation with α-nitroso-β-naphthol. The precipitate is voluminous and coloured, and the reaction therefore serves for the detection of very small quantities of palladium.[48]

At least two exact methods are now available for the determination of vanadium in special steels which may also contain titanium, molybdenum, and large quantities of chromium.[49] As these methods, however, are necessarily complicated, attention may be directed to a simpler one which meets the very common case where titanium and molybdenum are absent and chromium is only a minor constituent.[50] In 1908, Fenton showed that dihydroxymaleic acid was a far more sensitive reagent for titanium than hydrogen peroxide, and had the further advantage that vanadium did not interfere.[51] Other very sensitive reagents for titanium have since been announced,[52] and Fenton's work received no attention until lately, when it was found that a combination of the peroxide test and Fenton's test afforded a very satisfactory method for the simultaneous estimation of titanium and vanadium, especially in silicates.[53] Weiss and Landecker's method for the separation of columbium and tantalum, even as modified by Hauser and Lewite,[54] seems dependent on conditions not yet defined, for it has again been subjected to adverse criticism. Its latest critics revert to the method of separation which depends on the insolubility of potassium tantalum fluoride and the solubility of the corresponding columbium compound. This method has not been without its critics, but important modifications have been introduced which are said to make the precipitation of tantalum quantitative, whilst a single re-precipitation suffices to free it from columbium.[55] The precipitates were tested for columbium by a new colorimetric method, which, unlike the gallotannic acid method, is not affected by the presence of tantalum, and serves for the estimation of 0·1 per cent. of columbium with an error not exceeding 5 per cent.[56]

Among papers dealing with the determination of the non-metallic constituents of commercial metals and alloys, the following may be mentioned. It has been shown that any oxygen in brass probably exists as zinc oxide, and therefore cannot be determined by

[48] W. Schmidt, *Zeitsch. anorg. Chem.*, 1913, **80**, 335 ; *A.*, ii, 440.
[49] *Ann. Report*, 1912, 208.
[50] C. R. McCabe, *J. Ind. Eng. Chem.*, 1913, **5**, 736 ; *A.*, ii, 987.
[51] *T.*, 1908, **93**, 1064. [52] *Ann. Report*, 1912, 209.
[53] J. W. Mellor, *Trans. Eng. Ceram. Soc.*, 1912–13, **12**, 33 ; *A.*, ii, 627.
[54] *Ann. Report*, 1912, 208.
[55] E. Meimberg and P. Winzer, *Zeitsch. angew. Chem.*, 1913, **26**, 157 ; *A.*, ii, 348.
[56] E. Meimberg, *ibid.*, 83 ; *A.*, ii, 251.

the methods adopted for determining oxygen in copper; for although the zinc oxide is reduced by hydrogen at a high temperature, in the cooler portion of the combustion tube the reverse reaction occurs.[57] It has since been found that reduction in carbon monoxide is successful except in presence of tin or nickel.[58] A recent method for the determination of carbon in steel depends on direct dry combustion and measurement of the carbon dioxide produced. It involves the use of costly and complicated apparatus, which is justified, however, by the ease and speed with which results of the highest accuracy may be attained by means of it.[59] Another method, almost equally quick, also depends on combustion in a limited supply of oxygen, followed in this case by absorption of the carbon dioxide in a definite volume of $N/10$-alkali hydroxide, the excess of which is then determined by titration with acid and phenolphthalein.[60] For the estimation of phosphorus in vanadium steels three new methods have been proposed. One depends on the separation of phosphorus from vanadium by precipitation as aluminium phosphate under closely defined conditions[61]; another depends similarly on separation as cerium phosphate,[62] the separation in either case being but a preliminary to a phosphorus determination by the molybdate method. The third method depends on the fact that, if vanadium compounds are reduced to the quadrivalent condition and means taken to prevent their re-oxidation, the precipitation of phosphoric acid as phosphomolybdate is complete, and the precipitate is uncontaminated by vanadium compounds.[63] It is stated that methods for the estimation of phosphorus in tungsten-bearing materials which start with an alkali fusion lead to the loss of at least two-thirds of the phosphorus. Methods suitable for use with every class of tungsten-bearing material, all of them methods involving prolonged treatment with acid, are described.[64]

Electrochemical Analysis.

Although the number of papers dealing with electrochemical analysis shows no falling off, there have been few striking developments this year. It is found that certain reducing agents increase

[57] T. Turner, *J. Inst. Metals*, 1912, **8**, 248; *A.*, ii, 148.
[58] T. West, *ibid.*, 1913.
[59] E. Szász, *Zeitsch. angew. Chem.*, 1913, **26**, 281, ; *A.*, ii, 621.
[60] H. de Nolly, *Chem. Engineer*, 1913, **18**, 30.
[61] C. F. Sidener and P. M. Skartvedt, *J. Ind. Eng. Chem*, 1913, **5**, 838; *A.*, ii, 979.
[62] E. W. Hagmaier, *Met. and Chem. Eng.*, 1913, **11**, 28.
[63] J. R. Cain and F. H. Tucker, *J. Ind. Eng. Chem.*, 1913, **5**, 647; *A.*, ii, 875.
[64] C. M. Johnson, *ibid.*, 297; *A.*, ii, 529.

the oxidising potential of the dichromate ion on platinum by amounts up to 0·2 volt. No other oxidising agent tried exhibits a similar effect. The potential increases up to the very end point of the reaction, and is highest when the dichromate concentration is least. A final drop of *N*/10-reducing agent often depresses the potential by 0·5 volt. These observations have suggested an improvement in the electrometric method of titrating dichromate and ferrous salts, which makes it both more rapid and more accurate than the ferricyanide method.[65] Hitherto lead has been estimated electrolytically only as peroxide on the anode. Conditions have now been determined under which it may be deposited quantitatively as metal on the cathode. Neither zinc, cadmium, iron, nickel, cobalt, nor manganese interferes, but copper, if present, is wholly deposited with the lead, whilst tin and antimony are incompletely deposited, and must therefore be absent.[66] The excellent method for antimony depending on its deposition from an electrolyte of sodium sulphide, potassium cyanide, and sodium hydroxide, is not available for the simultaneous deposition of tin and antimony, as tin is incompletely deposited from a sodium sulphide electrolyte. Similarly, the equally good method for tin, depending on deposition from the solution of its sulphide in ammonium polysulphide, as usually carried out, breaks down when antimony is present, since metallic antimony is appreciably soluble in ammonium sulphide. If, however, this second method be so modified that, towards the end of the electrolysis, the concentration of ammonia and ammonium sulphide becomes negligible, the deposition of antimony is quantitative. These conditions can be secured by electrolysing at boiling temperature, the ammonia and ammonium sulphide being expelled or oxidised to ammonium sulphate. The simultaneous deposition of tin and antimony is thus made easy. The separation of antimony from tin is a more difficult problem, but a method depending on precipitation of the tin as stannic hydroxide and electro-deposition of the antimony from a solution of calcium sulphide is capable of good results if somewhat cumbersome.[67] A method for the separation of copper from tungsten, which avoids the use of potassium cyanide, has been described, and a modification of it is possibly the first exact method for the electrolytic separation of copper from molybdenum.[68]

[65] G. S. Forbes and E. P. Bartlett, *J. Amer. Chem. Soc.*, 1913, **35**, 1527; *A.*, ii, 984.

[66] R. Gartenmeister, *Chem. Zeit.*, 1913, **37**, 1281; *A.*, ii, 1075.

[67] N. K. Chaney, *J. Amer. Chem. Soc.*, 1913, **35**, 1482; *A.*, ii, 987.

[68] W. D. Treadwell, *Zeitsch. Elektrochem.*, 1913, **19**, 219; *A.*, ii, 342.

Organic Analysis.

One qualitative reaction of general interest has been the subject of an important paper this year. It has been shown that the reaction between ferric chloride and alkali ferrocyanide is a time-reaction, which is retarded by high acid and saline concentrations. When testing for ferrocyanide in very dilute solutions, ferrous sulphate is a far more sensitive reagent. The pale colour of the ferrous solution allows the use of a large excess, which tends to carry the reaction to completion, and there is usually enough dissolved oxygen in the water to oxidise the ferrous ferrocyanide to Prussian blue, so that, with only traces of ferrocyanide present, the maximum intensity of colour is obtained instantaneously.[69]

It is known that the presence of water-vapour materially assists the combustion of difficultly combustible substances. The principle has now been applied with success to the estimation of carbon in organic substances, as well as in steel. Lower temperatures are necessary, and the method is especially useful in the analysis of explosive compounds and substances which form hard masses of carbon. Nitrogenous compounds, such as glycine, alanine, hippuric acid, and carbazole, may be burnt completely at comparatively low temperatures, without the necessity of mixing copper oxide with the substance in the boat.[70] Cerium dioxide distributed on asbestos is found to be an effective substitute for the platinised asbestos of Dennstedt. In addition to its cheapness, the catalyst has the further merit that it is not poisoned by arsenic or lead peroxide. Its sole disadvantage, as compared with platinum, lies in the fact that it retains an amount of sulphur which varies with the temperature of combustion, so that sulphur cannot be determined simultaneously with carbon, hydrogen, and halogens.[71] A direct method for the estimation of oxygen in organic compounds has been described. It depends on the fact that when an organic substance is heated in pure hydrogen and the products of the reaction are passed over charcoal at a white heat, the whole of the oxygen in the original compound is converted into water, carbon dioxide, and carbon monoxide. The water and carbon dioxide are absorbed in the usual manner, and the carbon monoxide is estimated by passing the residual gas through iodine pentoxide and absorbing the resulting carbon dioxide in soda-lime.[72]

Many substances when submitted to Zeisel's process for the determination of methoxyl groups fail to give satisfactory results unless

[69] D. Vorländer, *Ber.*, 1913, **46**, 181 ; *A.*, ii, 257.
[70] S. Hilpert, *ibid.*, 949 ; *A.*, ii, 432.
[71] J. Bekk, *ibid.*, 2574 ; *A.*, ii, 981.
[72] M. C. Boswell, *J. Amer. Chem. Soc.*, 1913, **35**, 284 ; *A.*, ii, 334.

heated with fuming hydriodic acid for several hours, in some cases more than twelve hours. The addition of acetic anhydride, as suggested by Herzig, effects an improvement in some cases, but not in all, and, as Herzig pointed out, the presence of a methoxy- and not a methylimino-group is only indicated with certainty when the theoretical quantity of methyl iodide is liberated in the normal time of one and a-half hours.[73] It is now found that, in most of these difficult cases, hydriodic acid of D 1·7 effects complete reduction in the normal time, provided a little phenol is present. Tetramethylellagic acid, the anomalous behaviour of which led Herzig to attempt the improvement of Zeisel's method, only yields to fuming acid even in presence of phenol, but with the exception of methyl nitroanisate, no substance tested has required more than one and a-half hours.[74] Reference may be made to a volumetric modification of Zeisel's method, based on decomposition of the alkyl iodide by heat and titration of the iodine thus produced. Account is taken of the fact that a little hydriodic acid is formed at the same time, and the method is sufficiently exact, but it is scarcely simple enough to displace the original method.[75]

Some years ago it was proposed to estimate carboxyl groups by measurement of the hydrogen sulphide which is evolved when even weak organic acids are brought into contact with a solution of potassium hydrogen sulphide saturated with hydrogen sulphide. The method has the advantage over the titration method that most lactones and alcohols, and phenols as such, are without effect, but with the apparatus hitherto in use, only roughly approximate results could be obtained.[76] Apparatus has now been devised which avoids every source of error that can be avoided. Of the remaining errors one is constant and positive, whilst the other is negative and variable in amount, according as the acid is mono- or di-basic. With dibasic acids, the errors nearly balance each other, but monobasic acids are consistently underestimated by 2·1 to 2·4 per cent.[77]

Since iodoform and carbon tetraiodide contain 96·7 and 97·7 per cent. respectively of iodine, the gravimetric determination of one of these compounds in presence of the other is practically impossible. This fact lends importance to a recent proposal for effecting the determination by a gasometric method. The method depends on the fact that 1 gram of iodoform yields 56·6 c.c. of gas when treated with silver nitrate solution, whereas 1 gram of the

[73] J. Herzig, *Monatsh.*, 1908, **29**, 295; *A.*, 1908, ii, 638.

[74] F. Weishut, *ibid.*, 1912, **33**, 1165; *A.*, ii, 78.

[75] A. Klemenc, *ibid.*, 1913, **34**, 901; *A.*, ii, 733.

[76] F. Fuchs, *ibid.*, 1888, **9**, 1132, 1143; 1890, **11**, 363; *A.*, 1889, 463.

[77] W. H. Hunter and J. D. Edwards, *J. Amer. Chem. Soc.*, 1913, **35**, 452; *A.*, ii, 535.

tetraiodide only yields 42·9 c.c. The reactions are different, iodoform yielding carbon monoxide and silver iodide quantitatively, whereas the tetraiodide gives rise to carbon monoxide, carbon dioxide, silver iodide, and silver iodate, in proportions which vary with the experimental conditions. Clearly, however, this gasometric method is independent of the exact course of the reaction, provided, as is the case, all the carbon appears either as carbon monoxide or dioxide.[78]

Reference was made last year to a method for the estimation of malic acid depending on the increase in rotation produced by treating the solution with uranyl acetate.[79] Since the specific rotation of *d*-tartaric acid is also increased by uranyl salts, the method is not available in the frequent cases where malic and tartaric acids are present together. A method has now been devised for estimating both acids in the same solution, which is based on the facts that the rotation of each is increased independently of the other by treatment with uranyl acetate under defined conditions, and that both acids can be oxidised quantitatively to oxalic acid by heating with alkaline permanganate. In the absence of other substances which yield oxalic acid on oxidation and cannot be removed before treatment with permanganate, the method gives excellent results.[80] Another recent method for the separate estimation of tartaric, malic, and succinic acids when occurring together depends on the fact that, under certain defined conditions (faint acidity and relatively low concentration of alcohol), all three acids are precipitated by lanthanum nitrate, whereas other conditions, also closely defined, determine the precipitation of tartaric acid alone, or of tartaric and malic acids. The method is volumetric, a standard solution of lanthanum nitrate being used and the end-point determined electrometrically.[81]

A third method for the estimation of tartaric and malic (and citric) acids when occurring together introduces no new principle, but combines some older methods with Kling's method for the estimation of tartaric acid. This method is available in presence of succinic acid.[82] Since it became recognised that precipitation as tricalcium citrate does not afford a trustworthy means of estimating citric acid, a method proposed some years ago by Denigès has attracted attention. This method depends on oxidation of the citric acid to acetonedicarboxylic acid, which is then precipitated

[78] M. Lantenois, *Compt. rend.*, 1913, **156**, 1629 ; *A.*, i, 696.
[79] *Ann. Report*, 1912, 213.
[80] P. B. Dunbar, *Eighth Inter. Cong. App. Chem.*, 1912, XXVI, 375 ; *A.*, ii, 802.
[81] P. Dutoit and M. Duboux, *Bull. Soc. chim.*, 1913, [iv], **13**, 832 ; *A.*, ii, 888.
[82] L. Mathieu and L. Ferre, *Bull. Assoc. Chim. Sucr. et Dist.*, 1913, **30**, 842 ; *Ann. Chim. anal.*, 1913, **18**, 352 ; *A.*, ii, 990.

as an insoluble mercury compound. At least three authors have reported adversely on it, but a volumetric modification of it, due to Beau, one of its earliest critics, is beginning to find its way into text-books. Within the year, Beau's modification has been shown to be quite untrustworthy, but at the same time a satisfactory method—not differing in principle from that of Denigès—has been at last devised. Malic, lactic, and salicylic acids interfere, but accurate results are obtained in presence of tartaric, succinic, oxalic, benzoic, acetic, phosphoric, and sulphuric acids.[83]

A recent study of the effect of temperature, acid concentration, and time on the bromination of phenol has made it possible to estimate phenol with an error not exceeding 0·05 mg., and has also shortened the time necessary to make a determination, and shown that the large excess of reagents commonly used and supposed to be necessary may be decreased with advantage.[84] The authors of this work have also published a description of a method by which it is claimed that, in a mixture of phenol and the three cresols, the phenol, the *m*-cresol, and the sum of the *o*- and *p*-cresols can be calculated from the results of a single titration with iodine, provided that no other substance which reacts with iodine is present, and that if any other substance is present, the total content of phenols is known. The method is said to be accurate to within 0·2 per cent. for each constituent, but the published data do not bear out this claim. This is probably due to typographical errors, of which there are many obvious examples elsewhere in the paper, and it is to be hoped that the authors will publish some further notes on the method, which may be useful. This must depend to some extent on the time occupied in solving five simultaneous equations, a point which would be made more clear by a worked example.[85]

A recent paper on the estimation of some organic substances (mainly phenols and derivatives of phenols) from their consumption of alkaline permanganate[86] recalls three papers of wider scope by Hetper. The limitations of methods depending on the use of permanganate are obvious, but not only do they serve for the estimation of many substances in pure aqueous solution, but they have helped to solve some difficult problems, such as the separate estimation of citric, tartaric, and malic acids when occurring together. In any future attempt to make use of permanganate in complex cases like these, much time might be saved by reference to

[83] L. Gowing-Scopes, *Analyst*, 1913, **38**, 12; *A.*, ii, 162.

[84] L. V. Redman, A. J. Weith, and F. P. Brock, *J. Ind. Eng. Chem.*, 1913, **5**, 389; *A.*, ii, 632.

[85] *Ibid.*, 831; *A.*, ii, 988.

[86] C. M. Pence, *ibid.*, 218; *A.*, ii, 350.

Hetper's work, which not only covered a large number of organic substances, but was systematic, and therefore suggests the probable behaviour of many substances not actually tried.[87]

A paper by Ogilvie, on the use of invertase instead of acid for hydrolysing sucrose in commercial products when carrying out the Clerget method, was briefly referred to in the report for 1910.[88] By taking advantage of a recent proposal of Pellet's for improving the ordinary Clerget process, Ogilvie improved on the invertase process of Ling and Baker, who were the first to indicate the possible value of inversion with invertase in the analysis of low grade products of the sugar factory, and described experiments which confirmed the view of these authors that invertase is a selective hydrolyst, inverting only the sucrose (and raffinose if present) without at all affecting the non-sugar substances. At the same time it was shown that Andrlik's modification of the ordinary Clerget process gave results identical with those obtained by the invertase method, as did Pellet's sulphurous acid process, which is more convenient, whereas the ordinary Clerget-Herzfeld process gave results with beet molasses which were from 0·5 to 1·5 per cent. too low.[89] The investigation has now been extended to cane molasses, which yield identical results, whether examined by the invertase method or by the methods of Andrlik or Pellet, but render results which are from 0·4 to 1·3 per cent. too high when submitted to the Clerget-Herzfeld process. Whereas the error of the Clerget-Herzfeld method, when applied to beet products, is due to the presence of amino-acids that have a lower rotation in alkaline than in acid solution, the error —opposite in sense—with cane molasses is due to the fact that in presence of basic lead acetate the dextro-rotation of a cane molasses solution is increased, owing to the effect of the reagent on the lævulose always present.[90] Further notes on Pellet's sulphurous acid method, which, as originally described, did not give correct results, have been published, and its advantages, as compared with Andrlik's process, emphasised.[91] A new test for the detection of artificial invert sugar in honey has been described. Like Fiehe's test,[92] it depends on the presence of derivatives of furfuraldehyde in all artificial invert sugar, but it is claimed that it is somewhat more sensitive than Fiehe's test.[93]

[87] J. Hetper, *Bull. Acad. Sci. Cracow*, 1910, A., 601 ; *A.*, 1911, ii, 331 ; *Zeitsch. anal. Chem.*, 1911, **50**, 343 ; *ibid.*, 1912, **51**, 409 ; *A.*, 1912, ii, 811.

[88] *Ann. Report*, 1910, 174.

[89] J. P. Ogilvie, *J. Soc. Chem. Ind.*, 1911, **30**, 62 ; *A.*, 1911, ii, 232.

[90] J. P. Ogilvie, *Intern. Sugar J.*, 1912, **14**, 89 ; *A.*, 1912, ii, 393.

[91] *Ibid.*, 624.

[92] *Ann. Report*, 1910, 174 ; 1911, 174 ; 1912, 215.

[93] F. M. Litterscheid, *Chem. Zeit.*, 1913, **37**, 321 ; *A.*, ii, 351.

As was the case last year,[94] the only paper to be recorded, in connexion with the cryoscopic method for the detection and approximate estimation of added water in milk, is dated from Australia,[95] but, although nothing has yet been published here, it is satisfactory to be able to record that the possibilities of the method are now being investigated in this country.

Polenske's method of detecting beef and mutton fat in lard by the difference between the melting and solidifying points of the fats[96] has been shown to depend mainly on the fact that the α-palmitodistearin of lard has a "difference" value of 18·4, whilst the β-palmitodistearin of beef and mutton fat has a "difference" value of 11·8. Tristearin has a very high "difference" value (19·7), but the amount of tristearin in beef fat is not sufficient to outweigh the greater proportion of α-palmitodistearin in lard.[97] The very difficult problem of determining the relative proportions of cocoanut oil and palm kernel oil in mixtures of these two oils with a third (margarine mixtures) forms the subject of a recent paper, which describes a new method, which is not claimed as an exact method of analysis, but which has the merit of being independent of any assumptions as to the nature of the third constituent. In point of accuracy, it is probably not greatly, if at all, inferior to methods of this class.[98] The introduction of hardened (hydrogenised) fats has considerably limited the conclusions which may legitimately be drawn from the results of analysis of any fatty mixture. When nickel is present, there is a strong presumption that the mixture includes a hardened fat, and methods for the detection of minute amounts of nickel have been improved. Failure to detect a metallic catalyst, however, is by no means evidence that a hydrogenised fat is not present, and there is reason to believe that before long hardened fats, free from any trace of metallic catalyst, will appear in commerce, if they have not already done so.

In the absence of any other good method for the detection and estimation of glyceryl acetate in essential oils, attention may be directed to a method which depends on the separation of the glycerol and its estimation by the triacetin method.[99] The only other method available is one described in one of Schimmel's reports, which is less convenient, probably less trustworthy, and seems to have escaped the attention of abstractors of that document of 200 pages.

[94] *Ann. Report*, 1912, 214.
[95] J. B. Henderson and L. A. Meston, *Proc. Roy. Soc. Queensland*, 1913, **24**, 165.
[96] E. Polenske, *Arbeit. Kaiserl. Gesundh.-Amt.*, 1907, **26**, 444.
[97] A. Bömer and R. Limprich, *Zeitsch. Nahr. Genussm.*, 1913, **25**, 367 ; A., ii, 444.
[98] H. R. Burnett and C. Revis, *Analyst*, 1913, **38**, 255.
[99] S. G. Hall and A. J. Harvey, *J. Soc. Chem. Ind.*, 1913, **32**, 61 ; *A.*, ii, 253.

In a report on the present state of rubber analysis, made to the Sixth Congress of the International Association for Testing Materials in 1912, Hinrichsen recommends that, in the present state of our knowledge, caoutchouc should still be estimated by difference,[1] but since that date he has himself done much to improve the direct method, which depends on the formation of a tetrabromide of caoutchouc.[2] The improvement consists mainly in carrying out the reaction in chloroform solution, cooled by ice. Under these conditions, the proportion of bromine in the product is independent of the time of exposure to the action of bromine.[3] A modification of the nitrosite method[4] has been described. Briefly, it consists in determining the carbon content of the nitrosite by combustion analysis, and is therefore independent of the exact composition of the nitrosite, provided this contains all the carbon of the caoutchouc and no carbon from any other source. The method has given excellent results, but its author issues a warning that much further work is required before it can be generally recommended.[5] A new method depends on the action of sulphuric acid on caoutchouc in chloroform solution. The solution is violently agitated with concentrated sulphuric acid, poured into alcohol, and the precipitate, which is said to have the composition $(C_{10}H_{16})_{10},H_2O$, is washed with alcohol, dried at 100°, and weighed.[6]

A report on the testing of indigo-dyed or reputed indigo-dyed woollen and union fabrics may interest comparatively few, but is of great importance to those few, for the methods of analysis hitherto published afford no trustworthy means of estimating the quantity of indigo on a cloth in presence of other dyestuffs, and no method has yet been proposed for determining the quantity of the concomitant dyestuff. At the request of the Textile Institute these problems were made the subject of investigation at the University of Leeds and at the Technical College, Bradford, and as one result a new method of estimating indigo has been worked out, which is rapid, convenient of application, and gives accurate results even on heavy and dense cloths, whilst the results are unaffected by the presence of other dyestuffs. It is obvious that the simple statement of the percentage of indigo on a cloth does not afford to anybody but an expert an idea of the quality of the dye. What is required by manufacturers and merchants is a means of knowing what proportion of the total depth of colour is due to the indigo present. The solution of this problem might be expected to be difficult,

[1] F. W. Hinrichsen, *Chem. Engineer*, 1913, **18**, 165. [2] *Ann. Report*, 1911, 176.
[3] F. W. Hinrichsen and E. Kindscher, *Zeitsch. anorg. Chem.*, 1913, **81**, 70 ; *A.*, ii, 534. [4] *Ann. Report*, 1911, 176.
[5] L. G. Wesson, *J. Ind. Eng. Chem.*, 1913, **5**, 398 ; *A.*, ii, 631.
[6] R. Marquis and F. Heim, *Bull. Soc. chim.*, 1913, [iv], **13**, 862 ; *A.*, ii, 884.

having regard to the fact that the dyestuffs accompanying the indigo are not necessarily blue, but are frequently violet or red. The authors, than whom none could better assess in advance the magnitude of the task they had undertaken, state that it proved far more laborious than was anticipated. They have, however, worked out two methods, one of which is applicable even to the heaviest shades, and their results show that the maximum error of this method, in practised hands, is 7 per cent., a satisfactory degree of accuracy where no alternative method exists.[7]

Agricultural Analysis.

Reference was made last year[8] to the difficulty of preparing neutral solutions of ammonium citrate. Three methods have been described this year, each of which is said to be as exact as the method based on conductivity measurements at constant temperature. Of these three methods, that of Patten and Marti is incomparably the simplest. It depends on the estimation of the citric acid in the approximately neutral solution by titration with alkali in the presence of formaldehyde, and estimation of the ammonia by distillation with magnesia.[9]

The writer of last year's report on Agricultural Chemistry made it plain that before any material advance could be made in plant chemistry a thorough revision of analytical methods was necessary. Since then the estimation of carbohydrates in plant extracts has been the subject of special study at Rothamsted, and a paper has been published which concludes with a scheme for the estimation of dextrose, lævulose, maltose, sucrose, and pentoses in such extracts. Certain sources of error encountered in the estimation of sugars in plant extracts are dealt with, and prominence is given to the fact that asbestos, unless previously treated with sodium hydroxide, is liable to be attacked by Fehling's solution. This fact has been so long known to the writer that he supposed it was a matter of general knowledge, but the authors state that they have been unable to find any previous mention of it. This being so, they have undoubtedly performed a useful service in calling attention to the fact, and no apology is needed for giving further publicity to it here. Of the volumetric methods for the estimation of reducing sugars, that of Ling is found to be the most accurate as well as the most convenient. In dealing with plant extracts, owing to the accumulation of sodium acetate,

[7] A. G. Green and others, *J. Soc. Dyers*, 1913, **29**, 226, 227.

[8] *Ann. Report*, 1912, 218.

[9] J. M. Bell and C. F. Cowell, *J. Amer. Chem. Soc.*, 1913, **35**, 49; *A.*, i, 162; A. J. Patten and W. C. Marti, *J. Ind. Eng. Chem.*, 1913, **5**, 567; *A.*, ii, 790.

inversion of sucrose by citric acid of lower concentration than 10 per cent. is generally incomplete. Inversion by invertase is not interfered with by this salt. The only available method for the accurate estimation of maltose consists in the employment of maltase-free yeasts, such as *S. marxianus*, as suggested some years ago by Baker and Dick, who, however, did not succeed in making the method quantitative. This has now been done.[10]

The application to plant analysis of the hydrolysis of levulosans by acids is complicated by the fact that, in the presence of sulphuric acid and oxalic acid, at least 10 per cent. of the reducing sugars are destroyed before hydrolysis is complete, and, although in high concentrations of acetic acid, theoretical results may be obtained, the hydrolysis of inulin requires twelve hours, and the use of 10 per cent. of acetic acid introduces difficulties when the liquid is neutralised for the estimation of reducing sugars. The use of sulphosalicylic acid in moderate concentration is free from these objections.[11]

A paper on the non-nitrogenous "extractive" matters in fodder and foodstuffs is more important than its title might suggest, for the so-called non-nitrogenous extractive matters form a group of somewhat indefinite composition, and are estimated by difference. Moreover, the very term "extractive" matters is a misnomer, since many of these substances are not extracted directly, but are rendered soluble by hydrolysis more or less profound. In particular, the pentosans, hemicelluloses, and a portion of the lignin occur in various degrees of condensation, and may appear partly in the "extractives" and partly in the "crude fibre," according to the methods employed. Hitherto the author has appeared to be mainly concerned to show that his method for the determination of crude fibre ought to be preferred to other methods,[12] but the importance of this paper lies in the avoidance of controversial matters other than nominal ones, the recognition that a sharp separation of groups of various degrees of resistance is impossible, and the suggestion that, in these circumstances, the adoption of an international standard method is desirable, as making the results of different workers at least comparable. Not everyone will approve the author's terminology, but his facts are beyond dispute, and well marshalled to support his suggestion of an international method.[13]

[10] W. A. Davis and A. J. Daish, *J. Agric. Sci.*, 1913, **5**, 437.

[11] P. L. de Vilmorin and F. Levallois, *Bull. Soc. chim.*, 1913, [iv], **13**, 684 ; *A.*, ii 736.

[12] *Ann. Report*, 1912, 211.

[13] J. König, *Zeitsch. Nahr. Genussm.*, 1913, **26**, 273.

Physiological.

A method for the separate estimation of acetic, *iso*butyric, *iso*valeric, and α-methylbutyric acids in mixtures of all four acids owes its importance to the fact that these acids correspond with the most commonly occurring amino-acids which result from protein hydrolysis, and that the mixed amino-acids can be easily converted into the corresponding fatty acids. The method, therefore, gives quantitative information concerning the products of protein hydrolysis not readily obtainable by older methods. It depends on fractional moist combustion of the fatty acids by chromic acid. At 65° oxidation of secondary chains is completed, at 100° that of ketones to acids, whilst at 170° complete oxidation to carbon dioxide is reached. The determination of the carbon dioxide produced at each stage and the total acidity of the mixture give four data from which the percentage of each of the four acids in the mixture can be calculated.[14] A recent method for the estimation of amino-acids, peptides, and peptones depends on the fact that these substances dissolve cupric hydroxide quantitatively in the cold to form a metallic complex in a neutral or faintly alkaline solution, and an extension of the method permits of the rapid and accurate estimation of histidine in mixtures. This useful extension of the method depends on the fact that the copper complexes of amino-*n*-hexoic acid and of phenylglycine are so sparingly soluble that these acids will precipitate the copper from solution of all the other complexes examined (seventy in number), excepting that of histidine.[15] It has been shown that cystine and tyrosine can be completely separated by treatment with absolute alcohol saturated with hydrogen chloride. The tyrosine is converted into its ethyl ester, which dissolves, whereas the unaltered cystine remains undissolved. The separation by means of phosphotungstic acid is nearly as sharp, but in that case the cystine can never be recovered quantitatively from the precipitate.[16] Pyrrolidonecarboxylic acid may be separated from glutamic and other amino-acids by taking advantage of the fact that its silver salt is readily esterified by ethyl iodide, whereas, under similar conditions, glutamic acid, aspartic acid, asparagine, and proline remain unaltered.[17]

Ruhemann's triketohydrindene hydrate reaction[18] has been the

[14] K. Langheld and A. Zeileis, *Ber.*, 1913, **46**, 1171; *A.*, ii, 443.

[15] P. A. Kober and K. Sugiura, *J. Amer. Chem. Soc.*, 1913, **35**, 1546; *A.*, ii 990.

[16] R. H. A. Plimmer, *Biochem. J.*, 1913, **7**, 311; *A.*, ii, 806.

[17] E. Abderhalden and K. Kautzsch, *Zeitsch. physiol. Chem.*, 1912, **78**, 115; *A.*, 1912, i, 492.

[18] *Ann. Report*, 1911, 179.

subject of further studies. Its sensitiveness is even greater than was at first supposed, 1 part of glycine in 65,000 giving a distinct blue coloration.[19] A number of substances containing primary alcoholic, aldehydic, and ketonic groups give colour reactions on boiling with triketohydrindene hydrate, the coloration in the case of glycerol, dextrose, and amyl alcohol being blue, but these reactions occur only in highly concentrated and neutral solutions, and do not take place in dilute solutions or in the cold. In this and in other respects they differ from the reaction with amino-acids, which occurs in the cold and even in a vacuum.[20]

A method has been described by means of which oxycholesterol can be estimated in the unsaponifiable products obtained from tissues and other sources. This substance gives a colour reaction with a mixture of acetic and sulphuric acids, which is readily converted to a pure green colour by addition of a trace of ferric chloride. Solutions obtained in this way give a spectrum with a well-defined band in the red, the breadth of which is proportional to the amount of oxycholesterol in the solution. As the esters of oxycholesterol do not give the colour reaction, it is possible to estimate these by determining the amount of oxycholesterol present before and after hydrolysis.[21]

A novel suggestion for the estimation of urea in urine or blood is to convert it into ammonium carbonate by means of the urease of soy beans, and then to remove the ammonia in a current of air (Folin's method).[22] The ordinary hypobromite method has been subjected to renewed criticism, the authors of one paper contenting themselves with the observation that the results tend to be high, and recommending a blank test,[23] whilst another author has shown that the reaction does not proceed completely according to the generally accepted equation, but that part of the nitrogen is converted into oxygen compounds and part of the carbon is only oxidised to carbon monoxide. Of the conditions which influence the course of the reaction, the most important is the ratio of bromine to sodium hydroxide. Under certain conditions, stated in the paper, pure urea yields the theoretical volume of gas, although this gas is not pure nitrogen, but certain other constituents of normal urine evolve nitrogen on treatment with hypo-

[19] E. Abderhalden and H. Schmidt, *Zeitsch. physiol. Chem.*, 1913, **85**, 143; *A.*, ii, 643.

[20] W. Halle, E. Loewenstein, and E. Přibram, *Biochem. Zeitsch.*, 1913, **55**, 357; *A.*, ii, 992.

[21] I. Lifschütz, *ibid.*, **48**, 373; *A.*, ii, 350.

[22] E. K. Marshall, jun., *J. Biol. Chem.*, 1913, **15**, 487, 495; *A.*, ii, 991.

[23] L. Grimbert and M. Laudat, *J. Pharm. Chim.*, 1913, [vii], **7**, 569; *A.*, ii, 739.

bromite. This source of error can be reduced, but not entirely eliminated, by previous treatment with phosphotungstic acid, so that the results of the most careful work tend to be high. In the presence of dextrose the error is large, much carbon monoxide being formed and all the nitrogen appearing as such.[24]

G. Cecil Jones.

[24] M. Krogh, *Zeitsch. physiol. Chem.*, 1913, **84**, 379 ; *A.*, ii, 641.

PHYSIOLOGICAL CHEMISTRY.

Among the textbooks of the year, the first volume of the third edition of Abderhalden's "Lehrbuch,"[1] dealing with the chemistry and metabolism of proteins, fats, and carbohydrates, must be specially mentioned. The work has been re-written, and is indeed an entirely new book. It contains references to quite the most recent literature. The author claims to have consulted twenty thousand original papers in its preparation! It can only be said that the task of selection has been carried out with judgment, and the book is another instance of its author's almost miraculous capacity for labour. It gives a singularly suggestive presentation of the more important facts of a rapidly growing science.

The second volume of v. Fürth's new book[2] has appeared; it supplies an interesting account of digestion and metabolism. New editions of Biedl's "Innere Sekretion"[3] and of Czapek's "Biochemie der Pflanzen"[4] should be mentioned.

Each successive year brings proof that biochemistry is now attracting workers in rapidly increasing numbers. The output of papers in 1913 was very large, over five hundred researches being described in the *Biochemische Zeitschrift* alone. It is doubtful if really new ground has been broken. A retrospect of the year must for the most part deal with the development of enterprises begun before it opened. No paper, I think, has appeared which to a reviewer gifted with no more than ordinary insight suggests the opening of a new chapter in the science. Progress, nevertheless, has been very real.

If one were to endeavour to decide upon what is the most hopeful feature in the progress of the moment, I think it would be found in the increasing provision of accurate quantitative methods applicable to the determination of metabolites when present in minute amounts. For such methods physiological chemistry has long

[1] "Lehrbuch der physiologischen Chemie," Abderhalden, Urban und Schwarzenberg, Berlin and Vienna.

[2] "Probleme der physiologischen und pathologischen Chemie," Von Fürth, Vogel, Leipzig.

[3] Urban und Schwarzenberg.

[4] Gustav Fischer, Jena.

waited. When we want to study the equilibrium between the blood and tissues we have often, from the nature of the case, to deal with substances in trivial quantities, and determine variations which, although profoundly significant, may be very small. In the case of the blood we need, too, to be able to work upon a small amount of total material, because it so often is necessary to withdraw it from the living animal or from human individuals. The service rendered by Barcroft, Folin, Van Slyke,[5] Ivar Bang,[6] and others in providing trustworthy methods applicable under these conditions is extraordinarily great, as the haste on the part of others to use them has proved. Any lingering disbelief in the quantitative possibilities of microchemical methods must give way in face of accomplished facts.

Another very hopeful feature in current work is the proof it is bringing that the new physical chemistry, especially that chapter of it which relates to the mutual influence of colloids and electrolytes, is directly applicable to the study of the tissues whilst still living, and most fertile in explaining certain aspects of their behaviour. No one who reads, for instance, the papers of G. R. Mines, which deal with the physico-chemical properties of circulating media as they affect the beating heart, can fail to realise this. We recognise, too, that owing to the progress of physical chemistry, infinitely greater precision is being given to work done upon the blood and the other colloidal fluids from the body. If I may again quote in illustration of this English work alone, I would refer to recent papers by C. J. Martin and Harriette Chick.[7]

I have found it impossible to devote a special section of this report to progress made on these lines, although it has been great.

The Chemistry of Protein and Protein Metabolism.

Some not unimportant advances have been made towards the better definition of the properties of individual proteins, and some valuable evidence has accumulated bearing on the structure and configuration of the protein molecule, whilst our knowledge of the intermediary metabolism of proteins progresses in a satisfactory manner.

To illustrate the advances being made on the lines first mentioned, I may quote the work of L. L. Van Slyke and Bosworth[8] on caseinogen and casein. Having obtained these two proteins

[5] *J. Biol. Chem.*, 1913, **16**, 121 ; *A.*, ii, 1084.

[6] *Biochem. Zeitsch.*, 1913, **49**, 19 ; *A.*, ii, 446 ; *ibid.*, **51**, 193 ; *A.*, ii, 740 ; *ibid.*, **57**, 300 ; *A.*, 1914, ii, 75.

[7] For example, *Biochem. J.*, 1913, **7**, 318 ; *A.*, i, 915.

[8] *J. Biol. Chem.*, 1913, **14**, 231 ; *A.*, i, 660.

in a form especially pure (their preparations, unlike most samples of "pure" casein, were practically ash-free), they prepared first of all, by two distinct methods, a basic calcium salt of each. These compounds were neutral to phenolphthalein. However prepared, they showed a satisfactory constancy in their composition, which was such as to indicate that 1 gram of protein was in each case combined with 9×10^{-4} gram-equivalent of calcium.

It was next shown that, in the case of caseinogen, soluble compounds are formed with ammonium, sodium, and potassium, in which 1 gram of protein is combined with only 1·25 gram-equivalents of the base. With calcium, strontium, and barium, on the other hand, two sets of compounds are formed. Members of the first set are insoluble, and correspond in composition with the alkali compounds just mentioned, whilst in members of the second set, which are soluble, 1 gram of protein is combined with $2{\cdot}25 \times 10^{-4}$ gram-equivalent of calcium, etc. In the case of casein the interesting fact was demonstrated that although it yields compounds which in other respects correspond precisely with those of caseinogen, its molecule is in each case, except that of the basic compound first mentioned, combined with exactly twice the quantity of base. When, therefore, caseinogen is converted into casein under the influence of rennin its molecule would appear to be exactly halved. Judging from the percentages of base present in the various compounds described, and making certain assumptions as to the valencies of the proteins, the authors conclude that the equivalent weight of caseinogen is 8888, which agrees well with the figures obtained by calculation from its sulphur and phosphorus content. The equivalent weight of casein then becomes 4444. The quantitative work in this paper seems to be exceedingly satisfactory, and I quote it as an instance of the increasing precision with which such studies are being made.

In illustration of recent productive investigations into the constitution of protein, I will quote first the work of Dakin and Dudley[9] on racemised casein. This work, which followed similar studies made by Dakin on gelatin last year,[10] is essentially an extension of the yet earlier researches of Kossel and Weiss,[11] who showed that proteins, when digested at low temperatures with dilute alkali, undergo a rapid diminution of optical activity, which, however, is never completely abolished. Kossel and Weiss regarded the phenomenon as one of protein racemisation, and since on acid hydrolysis of the racemised material they obtained optically

[9] *J. Biol. Chem.*, 1913, **15**, 263, 271 ; *A.*, i, 1249.

[10] *Ibid.*, 1912, **13**, 357 ; *A.*, i, 208.

[11] *Zeitsch. physiol. Chem.*, 1909, **59**, 492 ; 1910, **68**, 165 ; *A.*, 1909, i, 542 ; 1910, i, 791.

inactive arginine, etc., they came to the interesting conclusion that certain of the protein *Bausteine* undergo racemisation much more readily when bound "intraprotein" than when free. Active arginine, for instance, is not affected in this sense by dilute alkali. Dakin advances a hypothesis to account for the facts, which seems entirely satisfactory. Supported by his own earlier observations on the contrasted behaviour of hydantoins and uramido-acids, he comes to the conclusion that racemisation occurs when the peptide linking exists, because there is then the possibility of keto-enol isomerism, of which the free amino-acids are incapable. The following formulæ, representing the equilibrium between the two forms of a peptide grouping, make this point clear:

$$\begin{array}{l} \mathrm{NH{\cdot}CO{\cdot}} \\ \mathrm{R{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CHR{\cdot}CO_2H} \end{array} \rightleftharpoons \begin{array}{l} \mathrm{NH{\cdot}CO{\cdot}} \\ \mathrm{R{\cdot}C{:}C(OH){\cdot}NH{\cdot}CHR{\cdot}CO_2H} \end{array}$$

When, under the influence of the alkali, the enol form is produced even to a small extent, racemisation must necessarily follow, since the asymmetry of the α-carbon atom is abolished. In these considerations another important point is involved. Of the two amino-acids concerned in the above peptide association, only that containing the ·CH·CO· group could exhibit keto-enol isomerism, and so undergo racemisation; that containing the free carboxyl group would remain unchanged under the influence of the dilute alkali. The condition of the latter represents that of the terminal members of any complex chain of linked amino-acids such as may exist in the protein molecule. Hydrolysis of a racemised protein should therefore lead to the appearance of both active and inactive amino-acids, the former being those of which the carboxyl groups originally shared in a peptide linking, the latter those of which the position was terminal in the peptide chains. When casein was racemised and afterwards submitted to acid hydrolysis, all the amino-acids obtained by Dakin and Dudley were inactive, with the exception of valine, leucine, and proline, and with the possible exception of alanine. The valine and leucine were partly in an active form, and the proline wholly so. In the case of racemised gelatin, Dakin had previously shown that glutamic acid and lysine are obtained active, although they are racemised by alkali when in the molecule of casein. There is a strong suggestion, therefore, that their relations are not the same throughout the molecules of gelatin and casein respectively.

In a further paper Dakin and Dudley[12] show that racemised casein is unattacked when submitted to the action of pepsin, trypsin, and erepsin. So completely resistant is it that no peptide linkings seem to remain in their original condition, otherwise

[12] *J. Biol. Chem.*, 1913, **15**, 271 : *A.*, i, 1278.

splitting at such linkings should occur. When given to an animal the racemised protein is excreted unchanged in the fæces.

Similar to the above in its bearings is the work of F. Obermayer and R. Willheim,[13] who have applied Sörensen's formaldehyde titration method, which has proved so extraordinarily useful in all work concerned with amino-acids, to a determination of the relative number of free amino-groups in different proteins. The quotient obtained by dividing the total nitrogen by the nitrogen of the terminal amino-groups they term the amino-index, and its value differs markedly in different proteins. It is, for instance, of the order of 21·5 in euglobulin and about 12 in albumin. In studying the bloods of widely different species they find marked differences in the amino-index of corresponding fractions, although results from the blood of the goose agree with those from fowls' blood, and horses' blood agrees with ox blood. The amino-index thus simply obtained will probably prove to be a characteristic stamp of an individual protein, and may assist as a criterion of purity when we are endeavouring to isolate individuals from protein mixtures.

Evidence concerning the constitution of proteins such as that offered by the two researches last quoted, although it may not yet carry us very far, comes, nevertheless, to the aid of the synthetic studies, which since Emil Fischer initiated them have gone on apace. One has but to glance at the recently published subject-index of the Journal of the Society to realise how actively the study of synthetic polypeptides is progressing, especially, but by no means exclusively, in the hands of Abderhalden and his co-workers. So much industry indeed and so much ingenuity are being brought to bear upon the problem that one may feel sometimes tempted to hope that the actual synthesis of a natural protein may be seen by the present generation. It is probably a far cry to that accomplishment, however, and it may be noted that Dakin and Dudley in the paper first quoted remark that their results raise a doubt as to whether it will ever be possible by existing methods to synthesise a naturally occurring protein. For treatment of compounds containing peptide linkings with alkali occurs in all these processes, and with large molecules of this character racemisation of the type dealt with would most probably occur. From the biological point of view, too, we must remember that the proteins of the tissues are very many and very diverse; colossal labours will have to precede the arrival of exact knowledge concerning the constitution and configuration of them all. Although even this knowledge must be available before descriptive biochemistry can

[13] *Biochem. Zeitsch.*, 1913, **50**, 369; *A.*, i, 668.

say its final word on protein equilibrium in the animal body, it is becoming increasingly sure that we shall not have to wait for such far-off knowledge before some of the most significant aspects of intermediary metabolism become clear to us. From some points of view, and those wide-embracing ones, we are entitled, it seems to me, to look upon the food proteins, and, no less, the proteins of the living tissues, as mere stores of amino-acids. The actual chemical dynamics of the body are concerned in the main with the latter as individuals. It is the physico-chemical properties of the intact tissue proteins rather than their exact constitution that concerns us at present. A preliminary hydrolysis, and that perhaps of the most complete kind, would appear to be the fate of all protein which is to undergo metabolism, whether the processes start in the gut or in the tissues. It is free amino-acids that enter the paths of significant change, and studies that have already proved highly profitable, and are likely to prove so for a long time to come, deal with the special fate of individual amino-acids in the body.

One may suggest here, in parenthesis, that it is perhaps because neither the intact molecule of protein nor complex polypeptides suffer oxidation, as such, in the body, that studies of protein oxidation *in vitro* have led to so little of physiological interest. Nevertheless, such studies continue, and doubtless deserve attention. O. Eisler,[14] continuing the work of v. Fürth, has described the results of oxidising casein and fibroin with potassium permanganate. One rather remarkable result was noted in the case of the latter substance. The chief oxidation product separated was a complex containing no less than 50 per cent. of its nitrogen in the basic form. The author compares this concentration of bases to what happens in the formation of protamines during the ripening of the testicle. The physiological application of the results seems, however, to be as remote as the chemistry of the process is obscure.

In previous reports Professor Halliburton has very fully reviewed the gradually accumulating evidence which shows the large part played in metabolism by liberated amino-acids. The matter must be further dealt with here because important work dealing with it has been carried out during the past year. Abderhalden,[15] for instance, has added yet another paper to a long series in proof of the ability of the animal to maintain itself when fed with a polypeptide-free mixture of amino-acids. This paper carries the air of finality, and would certainly seem to make any further evidence on the point quite unnecessary. The material fed was so

[14] *Biochem. Zeitsch.*, 1913, **51**, 26; *A.*, i, 777.
[15] *Zeitsch. physiol. Chem.*, 1913, **83**, 444; *A.*, i, 419.

thoroughly predigested as to contain no intact polypeptide material whatever. On this as its sole nitrogenous supply a dog lived in perfect health for one hundred days. During this period the animal gained 10 kilos. in body-weight, and, when the experiment closed there was nothing to suggest that it might not have been continued indefinitely. The dog was shaved before the special diet was given, and 76 grams of hair containing about 10 grams of nitrogen were removed. This had completely re-grown by the time the experiment was finished, and Abderhalden adduces the fact as an objective demonstration of protein synthesis! In this research, which was so conducted in all its details as to leave no loophole for criticism (the author fed and controlled the animal personally throughout), further proof was obtained of the fact that when tryptophan is removed the amino-acid mixture is no longer capable of maintaining the animal, and tyrosine was also shown to be necessary. Such observations as these will ultimately help us to decide exactly what amino-acids the body can, or cannot, synthesise for itself.

The work of O. Folin and W. Denis and that of D. D. van Slyke and G. M. Meyer, referred to in last year's report as giving such cogent proof of the fact that liberated amino-acids are absorbed as such from the intestine and reach the blood and tissues whilst still free and uncombined, has in each case been extended. Abderhalden,[16] who has long maintained a sceptical attitude in this matter, has now himself actually separated from the blood a number of individual amino-acids, and fully identified them. Needless to say, this accomplishment involved working on an enormous quantity of material. Folin and Denis[17] give us careful determinations of various forms of non-protein nitrogen in the blood of a great number of individuals, healthy and otherwise. Van Slyke and Meyer[18] have set themselves to trace the amino-acids as they leave the blood for the tissues, and, finally, to get information as to the locus of their transformation. It is already made clear that, in the case of such tissues as the muscles, the acids are merely absorbed from the blood without undergoing any immediate chemical change. When an increase occurs in the circulation the muscle can take up amino-acids until some 75 to 80 milligrams per 100 grams of their substance are present. At this point they become saturated, and remain for considerable periods in equilibrium with the blood. On the other hand, in the case of the liver there is a much larger initial increase (up to 150 milligrams per 100 grams), but the rise in the organ is followed by a period of

[16] *Zeitsch. physiol. Chem.*, 1913, **88**, 478.
[17] *J. Biol. Chem.*, 1913. **14**, 29; *A.*, i, 310.
[18] *Ibid.*, 1913, **16**, 197, 213, 231; *A.*, 1914, i, 104, 105.

rapid fall, during which urea increases in the blood. There can be little doubt, therefore, that the liver plays a prominent part in the more general course of amino-acid katabolism. The free amino-acids present in the tissues do not disappear during prolonged starvation, but tend rather to increase above the normal mean. The supply must therefore be kept up from the tissues themselves. Autolysis must occur *in vivo*, and, even in the case of tissue proteins, metabolism begins with the liberation of their *Bausteine*. As regards the katabolic breakdown of amino-acids the year has contributed something to the interesting collection of facts in our possession. H. D. Dakin and H. W. Dudley [19] state that all amino-acids undergo dissociation in solution into α-ketonic aldehydes and ammonia:

$$R{\cdot}CH{\cdot}NH_2{\cdot}CO_2H \rightleftarrows R{\cdot}CO{\cdot}CHO + NH_3.$$

If this be so, the production of the corresponding keto-acid, which is now so universally recognised as the first stage in the breakdown of an amino-acid in the body, is merely the direct oxidation of an aldehyde. In connexion with the further stages of change, Dakin [20] has examined several previously untried amino-acids with respect to their capacity, on the one hand, of yielding dextrose when given to a diabetic animal, and, on the other, of acting as precursors of acetoacetic acid when perfused through the liver. Seventeen have now been tested in this way, and the interesting fact has come to light that those which yield sugar do not yield acetoacetic acid, and those which give the latter are incapable of being converted into dextrose. Some of the protein *Bausteine* follow, therefore, the path of carbohydrate metabolism, whilst others ultimately join the path taken by fatty acids. Another very small group seems to enter on neither of these paths. In connexion with the special fate of phenylalanine, the work of Embden and Baldes [21] has given unexpected results. Phenylpyruvic acid does not yield acetoacetic acid in the liver, and so is probably not, as analogy would suggest it should be, the normal primary oxidation product of phenylalanine. Oxidation would seem first to occur in the ring, for *l*-α-phenylalanine, when perfused through the liver, gives rise to normal *l*-tyrosine, so that further breakdown would be on lines pertaining to the latter, a most interesting fact. The metabolic significance of the phenylalanine contained in any protein would seem to be identical with that of its tyrosine, if the former is in this way first converted into the latter.

[19] *J. Biol. Chem.*, 1913, **14**, 558; *A.*, i, 925.
[20] *Ibid.*, 321; *A.*, i, 671.
[21] *Biochem. Zeitsch.*, 1913, **55**, 301; *A.*, i, 1279.

The realisation of the fact that each constituent of protein has special relations in metabolism and may subserve a special purpose in the body, adds more than a purely chemical interest to the discovery of new amino-acids in the protein molecule. We have fully realised that the tale of these was probably not complete, but it is rather startling to find that the year has offered some evidence for the existence of no less than three additional ones. Abderhalden and Weil[22] have obtained from the proteins of nervous tissues the straight-chain isomeride of leucine (α-amino-*n*-hexoic acid), which they propose to call norleucine. Foreman[23] has given evidence for the existence of an α-aminobutyric acid in casein, and M. Guggenheim[24] has separated from the tissues of *Vicia faba* an acid which is almost certainly 3:4-dihydroxyphenyl-α-aminopropionic acid. Although the latter was not obtained by hydrolysis of protein, there can hardly be a doubt that it arises from autolysis of the proteins of the plant.

A few words may now be given to a quite different aspect of the protein question. A desire to discover what is the minimum amount of protein on which the human body can maintain itself is still in the minds of many. In a research carried out by Hindhede[25] at Copenhagen, nitrogenous equilibrium, and, apparently, good health, were maintained in certain individuals on an extraordinarily low intake. In the case of one person, Madsen, a diet consisting almost wholly of potatoes and margarine was well borne. On this diet and under average conditions of activity the protein consumption necessary for equilibrium was only 19 grams daily. In the presentation of such facts there is usually an unnecessary assumption that the low intake is physiologically virtuous. We may set against Hindhede's research, however, an extraordinarily interesting study of the dietetic habits of Esquimaux by A. and M. Krogh.[26] Here in actual quantitative experiments we find individuals consuming over 500 grams of protein daily, with results entirely satisfactory to themselves, and yet this experimental consumption fell far below that of individuals free to follow their instincts! We find in these two researches noteworthy evidence of the wide ranges to which the body can adjust itself. It is quite sure that the physiological optimum of protein can only be defined in relation to personal and racial peculiarities, as well as habits and environment.

[22] *Zeitsch. physiol. Chem.*, 1913, **88**, 272; *A.*, 1914, i, 20.
[23] *Biochem. Zeitsch.*, 1913, **56**, 1; *A.*, i, 1249.
[24] *Zeitsch. physiol. Chem.*, 1913, **88**, 276; *A.*, 1914, i, 49.
[25] *Skand. Archiv. Physiol.*, 1913, **30**, 97.
[26] *Meddelelser om Groenland*, 1913, **51**; *A.*, 1914, i, 106.

Purine Metabolism.

The extraordinary activity which has been displayed in quite recent years in connexion with the constitution of the nucleic acids and the related subject of purine metabolism has for the moment diminished. I need quote only a few papers. H. Steudel[27] has begun a study of the nucleohistone of Lilienfeld, which is likely to add accuracy to our knowledge of that substance. He confirms exactly the original account of its composition, although without claiming that this confirmation proves it to be a chemical individual; he shows that it contains no other phosphorus than that present in true nucleic acid. M. Dohrn[28] has described a somewhat slight research on the effect of feeding thymus-nucleic acid to a young man. The only point of significance in the results was that the urea nitrogen was unaffected. The increase in the uric acid nitrogen represented under 10 per cent. of the basic nitrogen given, and the rest was not recovered. Nevertheless, the excess phosphorus excretion was proportionate to that present in the nucleic acid given. As emphasising the exceptional position of man in excreting unoxidised uric acid rather than allantoin, we have the work of A. Hunter and M. H. Givens.[29] They show that even the monkey (*Cercopithicus*) departs from the human type of purine metabolism and excretes allantoin. The same observers[30] have greatly added to the list of species studied in this connexion, and find that the power to oxidise uric acid is possessed by the following groups in decreasing degree: Carnivora, rodents, ungulates, marsupials, man. E. R. Long[31] finds that the ferment adenase is absent from the human liver, and could discover none in individual fœtal tissues. In some cases it is certainly present in the fœtus, as experiments with an emulsion of the whole body showed, but it could not be localised. Certainly the most important paper of the year bearing in any way on purine metabolism is that by Folin and Denis already quoted. It is full of suggestive points. Among them we may note the most interesting fact that human blood contains several times as much uric acid as does the blood of any other animal examined. This corresponds with the higher excretion in the case of man. In the case of gout, however, we may have much larger quantities circulating than normal without increased excretion, showing, in Folin's opinion, a failure on the part of the kidneys. This failure must be related specifically

[27] *Zeitsch. physiol. Chem.*, 1913, **87**, 207 ; *A.*, i, 1116.

[28] *Ibid.*, 1913, **86**, 130 ; *A.*, i, 1016.

[29] *J. Biol. Chem.*, 1913, **13**, 371 ; *A.*, i, 126.

[30] *Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxiv–xxv ; *J. Biol. Chem.*, **14** ; *A.*, i, 558.

[31] *J. Biol. Chem.*, 1913, **15**, 449 ; *A.*, i, 1272.

to uric acid, for other non-protein nitrogenous substances may be normal in the blood of gouty individuals.

The Metabolism of Carbohydrates and Fats.

In the endeavour to establish the successive steps involved in the breakdown of the dextrose molecule in the body, most workers have regarded cleavage into a molecule containing three carbon atoms as being the first step involved. As there is now no reasonable doubt that one line at least of carbohydrate katabolism passes through the stage of lactic acid, recent work on the question has been largely concentrated on a search for the precursors of that acid. Many facts already acquired point to glyceraldehyde as being in all probability the first-formed product from sugar; for the moment the evidence in favour of this, although cogent enough, remains in the main of an indirect character. Meanwhile, during the past year, certain very striking researches have awakened interest in those substances which represent intermediary stages between glyceraldehyde and lactic acid; in particular, attention is being drawn to pyruvaldehyde (methylglyoxal) and pyruvic acid, both of which can, of course, be obtained from dextrose by chemical means. Early in the year Dakin and Dudley [32] published the noteworthy observation that tissue extracts acting at body temperature rapidly convert methylglyoxal into lactic acid:

$$CH_3{\cdot}CO{\cdot}COH + H_2O \longrightarrow CH_3{\cdot}CH(OH){\cdot}CO_2H.$$

Almost immediately after Dakin's publication C. Neuberg [33] confirmed the observation on independent lines, whilst P. A. Levene and G. M. Meyer [34] showed that intact leucocytes brought about the same change. Later Dakin showed that the keto-aldehyde yields lactic acid when perfused through the isolated liver.

To complete the account of the relationships which exist, it must be first stated that Dakin obtained the dinitrophenylhydrazone of methylglyoxal from lactic acid by simply mixing solutions of the latter with nitrophenylhydrazine, whilst he proved that methylglyoxal yields dextrose when administered to a glycosuric animal, just as does lactic acid itself. Alanine also, as we have seen, yields methylglyoxal with readiness. The biological significance of this keto-aldehyde can therefore scarcely be in question, and the following equilibrium relations probably obtain in metabolism, the reactions involved being reversible:

$$\begin{array}{c} C_6H_{12}O_6 \\ \downarrow\uparrow \\ CH_3{\cdot}CH(OH){\cdot}CO_2H \rightleftharpoons CH_3{\cdot}CO{\cdot}CO_2H \rightleftharpoons CH_3{\cdot}CH(NH_2){\cdot}CO_2H. \end{array}$$

[32] *J. Biol. Chem.*, 1913, **14**, 155; *A.*, i, 565.
[33] *Biochem. Zeitsch.*, 1913, **51**, 484; *A.*, i, 927.
[34] *J. Biol. Chem.*, 1913, **14**, 551; *A.*, i, 932.

The direct derivation of lactic acid from methylglyoxal involves the addition of a molecule of water, a process which in this case we ought perhaps to regard (as Neuberg suggests) as a kind of "internal Cannizzaro's reaction." If, on the other hand, pyruvic acid should prove to emerge as an intermediate metabolite between methylglyoxal and lactic acid, there would clearly be a significant difference in the chemical mechanisms involved. Biological interest in pyruvic acid has been awakened by Neuberg's observation that it is easily fermentable by yeast, and by the fact that being the keto-acid corresponding with alanine it might well be expected to appear in metabolism. G. Embden and M. Oppenheimer[35] find that it yields lactic acid when perfused through a glycogen-free liver. P. Mayer[36] was unable to obtain any increase of sugar as a result of administering it to phloridzinised dogs. A. I. Ringer, E. M. Frankel, and L. Jonas[37] obtained some increase, but as it was small compared to the sugar produced from either alanine or lactic acid in similar circumstances they concluded that pyruvic acid is unlikely to be an obligatory stage in the conversion of alanine into lactic acid. Dakin and Janney[38] agree with this conclusion, and hold that in so far as pyruvic acid is a precursor of sugar in the body, it is because it may be directly reduced to lactic acid, which then passes by way of methylglyoxal to dextrose. Many points of interest in the papers just referred to cannot be dealt with here. It is clear that more experimental work is necessary to render the metabolic relations between dextrose and lactic acid certain; but the very fact that the current work here, as elsewhere in studies of intermediary metabolism, is now able to deal with details shows how much progress has been made.

The importance of the influence of the pancreas in carbohydrate metabolism has been before us for so many years that it is disappointing to feel that we are still in the dark as to how it is exerted. Experiments dealing with the sugar consumption of the heart from normal and de-pancreatised animals respectively seemed to show quite definitely that the pancreatic factor was active at the locus of utilisation, but Starling and his co-workers now find that these experiments give inconclusive results. First of all, E. W. H. Cruickshank[39] finds that the heart of the de-pancreatised animal is apt to contain more than a normal amount of glycogen, and S. W. Patterson and E. H. Starling[40] find that the

[35] *Biochem. Zeitsch.*, 1913, **55**, 334; *A.*, i, 1275.
[36] *Ibid.*, 1913, **49**, 486; *A.*, i, 564.
[37] *J. Biol. Chem.*, 1913, **15**, 145; *A.*, i, 937.
[38] *Ibid.*, 177; *A.*, i, 937.
[39] *J. Physiol.*, 1913, **47**, 1; *A.*, i, 1268.
[40] *Ibid.*, 137; *A.*, i, 1263.

energy necessary for its work may be obtained from this internal store. This explains why in earlier experiments there was no consumption of sugar from the circulating medium. Although the further experiments of Cruickshank and Patterson[41] on the heart of the cat seem to point to a certain degree of diminution in the carbohydrate metabolism of the diabetic heart, the total evidence remains inconclusive; Starling, indeed, is inclined to abandon the view that the essential or, at any rate, the primary factor in diabetes is the absence of power on the part of the tissues to consume sugar.

The above evidence concerning the pancreas is supported by the observations of J. R. Murlin and B. Kramer,[42] who were unable to obtain as the result of injecting pancreatic extracts into de-pancreatised dogs any specific effect on the dextrose–nitrogen ratio, or on the respiratory quotient which could be interpreted as an index of increased combustion of carbohydrate. This was also the experience of F. Verzár and A. von Fejér.[43] A. Gigon and M. Massini,[44] using the older technique of Cohnheim, were also unable to discover that the addition of pancreas preparations had any effect in increasing the power of crushed muscles to destroy (? polymerise) sugar. The work of the year seems to suggest on the whole that the pancreas is concerned in stabilising the carbohydrate sources of the body rather than in promoting the actual utilisation of sugar. Verzár and Fejér[45] state that the intravenous injection of sugar at the height of the diabetes due to the removal of the pancreas has no effect whatever on the respiratory quotient, and they advance this as sufficient proof of the fact that no trace of sugar oxidation occurs. It is extraordinary if, in the absence of its pancreas, the otherwise intact animal is really wholly unable to use sugar, that isolated organs from the same animal can apparently use it. An explanation of this paradox would, it seems to me, carry much of importance in its train.

In connexion with the influence of other glands on carbohydrate equilibrium, I have space only to mention one very interesting research. L. H. Weed, H. Cushing, and C. Jacobson[46] have shown that stimulation of the cervical sympathetic nerve, or of the "sugar centre" in the bulb, liberates a hormone from the posterior lobe of the pituitary body, which causes glycogenolysis and glycosuria. They excluded any possibility of the effect being due to a direct nervous stimulation of the muscles or viscera.

[41] *J. Physiol.*, 1913, **47**, 381.
[42] *J. Biol. Chem.*, 1913, **15**, 365; *A.*, i, 1268.
[43] *Biochem. Zeitsch.*, 1913, **53**, 140; *A.*, i, 1022.
[44] *Ibid.*, 1913, **55**, 189; *A.*, i, 1270. [45] *Loc. cit.*
[46] *Amer. J. Physiol.*, 1913, **31**, xiii–xiv; *A.*, i, 309.

No point in the history of carbohydrate metabolism is more interesting than that at which in a somewhat mysterious manner it trenches upon the metabolism of fat. The standing question as to why the oxidation of fatty acids fails to go to completion when carbohydrates or derivatives from carbohydrates are, for this or that reason, not available, was never more to the forefront than now. A solution of this puzzle is, indeed, much called for, and would be a gain to practical medicine as well as to physiology. We cannot be content any more to rest upon such phrases as "fats only burn in a fire lit by carbohydrates," and the like; we want an explanation in terms of understandable chemical reactions, and it may be said that most of the attempts to get at the details of carbohydrate and fat metabolism are converging upon this particular problem. Many papers of the year have been concerned with it directly or indirectly, but I have only space to mention a few. Those I have chosen are not necessarily the most interesting, but they contain points which are more or less new. The aceto-acetic acid which arises from successive β-oxidations of the physiological fatty acids, and from certain amino-acids (see above), is normally, of course, further changed in the body, but not if carbohydrates are absent, and not if the tissues are unable to use carbohydrates efficiently, as in diabetes. Then we have the condition of acidosis, in which unaltered acetoacetic acid circulates in the blood. In explanation, some have thought of the possibility of a condensation occurring between the keto-acid and aldehydes derived from carbohydrates, a combination yielding possibly a more readily oxidised substance. This year one worker at least has postulated a combination before breakdown, and having prepared fatty acid esters of dextrose, has decided their physiological properties. But the results of the research do not allow of any very definite conclusion being based on them.[47] Another possibility has, however, been advanced in explanation or partial explanation of the facts. It was shown last year by A. Loeb,[48] working under the inspiration of Embden, that acetoacetic acid can arise in the liver, not only from the oxidations of the higher fatty acids, but also by synthesis from acetić acid itself. E. Friedmann[49] showed that this only occurs when the liver is rich in glycogen, a point which has now been confirmed by G. Embden and A. Loeb,[50] and it is clear that it is one of significance in connexion with the problem we are considering. Friedmann suggests that acetoacetic acid is formed from acetic acid by condensation of the latter with

[47] W. R. Bloor, *Eighth Inter. Cong. App. Chem.*, 1912, XIX, 29; *A.*, i, 1014.
[48] *Biochem. Zeitsch.*, 1912, **47**, 118; *A.*, i, 130.
[49] *Ibid.*, 1913, **55**, 436; *A.*, i, 1276.
[50] *Zeitsch. physiol. Chem.*, 1913, **88**, 246; *A.*, i, 1411.

acetaldehyde to yield crotonic acid as an intermediate product, and J. Mochizuki [51] has carried out experiments which seem indirectly to confirm this. Embden, however, shows reasons for believing that the simple equilibrium:

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H + H_2O \rightleftarrows 2CH_3{\cdot}CO_2H$$

obtains. In either case it is obvious that the removal of acetic acid from the liver cell would favour the breakdown of acetoacetic acid. Now acetylation is a process of which the body has been proved capable, and the suggestion is that carbohydrate products may undergo this process, and so encourage the progress of the above reaction in the required direction. The facts offer at least a definite suggestion, and should encourage further research. Whether the successive removal of two carbon atoms which occurs during the course of β-oxidation in fatty acid chains really results in the production of acetic acid at each step, which would make the latter a very prominent metabolite, is yet to be proved or disproved. If it were the case, the importance of the above equilibrium relation would be very great.

Lipoids.

Much attention has been given of late to the lipoids of the brain. Towards the end of last year S. Fränkel, P. Kirschbaum, and K. Linnert [52] gave an account of the distribution of cholesterol in that organ, and J. L. Smith and W. Mair [53] have published elaborate analyses showing the proportions of various lipoids in the human brain at different ages. Further valuable analytical data are contained in a paper by C. Serona and A. Palozzi.[54]

The pure chemistry of the cerebrosides [55] and phosphatides from nervous tissues, although still suffering from some vagueness, both as regards facts and nomenclature, is making good progress. In particular some careful work has been done on the cerebrosides (galactosides).[56] A. Lapworth has dealt successfully with the purification of the most prominent among them—cerebrone—and has thrown fresh light on the constitution of its basic constituent, sphingosine. The most important acid obtained on hydrolysis of the mixed cerebrosides from the brain is cerebronic acid, ($C_{25}H_{50}O_3$). This has been the subject of further study by Levene [57] and his

[51] *Biochem. Zeitsch.*, 1913, **55**, 443; *A.*, i, 1277.
[52] *Ibid.*, 1912, **46**, 253; *A.*, i, 128.
[53] *J. Path. Bact.*, 1913, **17**, 418; *A.*, i, 313.
[54] *Arch. Farm. sperim.*, 1913, **15**, 375; *A.*, i, 1410.
[55] *Ann. Report*, 1908, 234.
[56] *T.*, 1913, **103**, 1029.
[57] *J. Biol. Chem.*, 1912, **12**, 389; *A.*, 1912, i, 1007; *ibid.*, 1913, **14**, 257; *A.*, i, 587.

colleagues at the Rockefeller Institute. They have made it nearly certain that the substance is a normal α-hydroxypentacosoic acid. Another fatty acid, however, arises on hydrolysis of the cerebrosides. This has been separated during the past year by H. Thierfelder,[58] P. A. Levene,[59] and O. Rosenheim,[60] all working independently. It has the formula $C_{24}H_{48}O_2$. It arises from the more soluble of the cerebrosides, and, if we accept Thudichum's nomenclature, from kerasin; Thierfelder, regarding it as a new acid, gave it the name kerasinic acid. Levene, however, believes it to be identical with lignoceric acid, and Rosenheim has come independently to the same conclusion. The last-named author[61] has developed his method of extracting the cerebrosides by means of cold pyridine, which avoids any procedure likely to break down pre-existing complexes. He advances his results as yielding proof that these substances (which he proposes to call galactosides) exist free and uncombined in the brain. With regard to the phosphatides of nervous tissue we may note that J. Parnas[62] finds stearic acid to be the only saturated fatty acid contained in kephalin, whilst A. Baumann[63] and M. H. Renall[64] have independently shown that its basic constituent is aminoethyl alcohol. A somewhat striking contribution to the metabolic side of these substances is E. Salkowski's[65] finding that on giving kephalin by the mouth the amount of phosphatides in the brain is increased.

Cholesterol has received a considerable amount of attention during the year. At the riddle of its constitution Windaus and others continue to work, but no very important new facts have come to light, and I must not give space to the question. To the physiology of cholesterol J. A. Gardner[66] has made another contribution, this time in conjunction with P. E. Lander. Working with cats, they have obtained further evidence for the fact that the body deals in a highly conservative manner with its store of cholesterol, that which is excreted in the bile being re-absorbed and utilised afresh. An interesting point is found in the probability that the re-absorption occurs in the form of esters, at any rate, when the diet is rich in carbohydrates. Addition of cholesterol to the diet increases its amount in the blood, liver, and suprarenals, but not in the muscles, kidneys, or lungs, where the quantity is

[58] *Zeitsch. physiol. Chem.*, 1913, **85**, 35; *A.*, i, 747.
[59] *J. Biol. Chem.*, 1913, **15**, 359; *A.*, i, 1129.
[60] *Trans. Internat. Congress of Med.*, Sect. II, 626.
[61] *Biochem. J.*, 1913, **1**, 604.
[62] *Biochem. Zeitsch.*, 1913, **56**, 17; *A.*, i, 1253.
[63] *Ibid.*, 1913, **54**, 30; *A.*, i, 1041.
[64] *Ibid.*, 1913, **55**, 296; *A.*, i, 1254.
[65] *Ibid.*, 1913, **51**, 407; *A.*, i, 789.
[66] *Biochem. J.*, 1913, **1**, 576.

very constant. A special interest in this connexion is attached to the suprarenals. L. Wacker and W. Hueck [67] find a close parallelism between the amount of cholesterol in these glands and that in the blood, a relation which is maintained in spite of the wide fluctuations induced by disease. Gardner's results are in accordance with this, although he finds, as does Landau,[68] that in inanition there is accumulation in the blood, and almost a complete disappearance from the suprarenals. Wacker and Hueck find that the labile part of tissue cholesterol is that which exists as esters, and this (a suggestive point) is indicated by the work of others, including, I think, that of Gardner. F. Kauders [69] has published very full analytical data concerning the cholesterol and cholesterol esters contained in the serum and blood corpuscles of various animals. E. Schreiber and Lénárd [70] state that oxycholesterol is found in all organs of the body save the liver. I. Lifschütz [71] confirms this statement, and gives evidence in support of his belief that the substance undergoes further change in the last-mentioned organ.

The relations of cholesterol and the phosphatides to immunity phenomena, although still a subject which inspires much work, cannot be treated in this report. I have space only to deal with one other research. A. Mayer and G. Schaeffer [72] have shown that the kind and amount of lipoids present in a given organ are characteristic for that organ. They speak of lipocytic constants and indices such as the ratios: $\frac{\text{fatty acid}}{\text{phosphorus}}$ and $\frac{\text{cholesterol}}{\text{fatty acids}}$, which maintain a constant mean value in most organs other than the muscles, and are independent of the species.

Chemistry of Respiration.

Work on the pure chemistry of hæmoglobin has made considerable progress during the year, and most of those whose names we associate with the work have published papers. R. Willstätter and M. Fischer [73] have obtained from blood pigment the aetioporphyrin ($C_{31}H_{36}N_4$), which had been previously obtained from chlorophyll, so that this substance constitutes a definite linking between the

[67] *Arch. expt. Path. Pharm.*, 1913, **71**, 373; *A.*, i, 554.
[68] *Deutsch. med. Wochensch.*, 1913, **12**, 1.
[69] *Biochem. Zeitsch.*, 1913, **55**, 419; *A.*, i, 1258.
[70] *Ibid.*, 1913, **49**, 458; *A.*, i, 544.
[71] *Ibid.*, 1913, **52**, 206; *A.*, i, 932.
[72] *Compt. rend.*, 1913, **156**, 487; **157**, 156; *A.*, i, 424, 1017.
[73] *Zeitsch. physiol. Chem.*, 1913, **87**, 423; *A.*, i, 1257.

animal and the plant pigment, but we are warned by the authors that too much must not be made of the supposed close relation in their constitution. Important differences probably exist in their molecular structure. It is impossible to appraise properly in small space the work done in this domain. I must content myself with pointing out the interest and importance of the paper just mentioned. It gives a large amount of information concerning the present position of the subject, as well as much fresh work.

The physico-chemical and physiological properties of hæmoglobin and its relations with oxygen in the blood continue to receive illumination at the hands of J. Barcroft [74] and his co-workers. As is well known from their work, the dissociation curve of oxyhæmoglobin, as it exists in the blood, is very different from that of a pure solution, so potent is the influence of salts and of the carbonic acid in the former.

A. V. Hill [75] and Barcroft [76] have published papers in which the observed form of the blood dissociation curves receives extraordinarily satisfactory explanation.

The effect of variations in the hydrogen-ion concentration of the blood has proved to be of such practical importance that Barcroft has felt the necessity of introducing a new nomenclature in connexion with it. When the hydrogen-ion concentration is normal and the dissociation curve also normal, it is proposed to speak of the blood as *mesectic*. When, owing to a fall of acidity, the dissociation curve is displaced, more oxygen than normal being taken up at any given tension, the blood is *pleonectic*. With a rise of acidity the absorption of oxygen is proportionately less; then the blood is *meionectic*.

The effect of various conditions on the dissociation curve has been fully studied. Severe exercise, for instance, produces meionexy, even although the carbonic acid tension of the blood is reduced. This is because other acids formed in metabolism increase the hydrogen-ion concentration. On the other hand, living at high altitudes may leave the blood mesectic, the lowered carbonic acid tension being then nicely compensated by the formation of other acids. A high degree of meionexy, however, is produced by severe exercise under these conditions. The effect of moist heat, such as may exist in factories, etc., is to produce an uncompensated lowering in the carbonic acid tension; the blood then becomes pleionectic. The results of these researches show that in circumstances in which the blood is mesectic the subject feels in normal health, even although the blood may contain abnormal acids; whilst when

[74] *Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlv, xlvi, xlvii; *A.*, i, 306.
[75] *Biochem. J.*, 1913, **7**, 471; *A.*, i, 1250.
[76] *Ibid.*, 481; *A.*, i, 1250.

it is either pleionectic or meionectic the subject feels out of his normal condition, and betrays symptoms of the change which has taken place. These considerations are likely to prove of no small importance in practical medicine. A study carried out on the clinical side by T. Lewis and in the laboratory by Barcroft[77] and others has already shown that clinical cases exist in which dyspnœa is a prominent symptom, but from which an equivalent cyanosis is absent. The fundamental factor of these cases seems to be an increase in the proportion of acids (exclusive of carbonic acid) to bases in the blood, and the symptoms are really an expression of the consequent meionexy.

The nicety with which the hydrogen-ion concentration of the blood is regulated in normal circumstances is demonstrated by the researches of Haldane and his co-workers.[78] The kidney probably plays the chief part in this adjustment.

Whilst carbon dioxide as an acid determines the stability of oxyhæmoglobin, it would seem, to judge from experiments, which have as yet been only briefly reported,[79] that the presence of oxygen conversely diminishes the stability of carbonic acid compounds in the blood. As a result of this relation, the velocity of evolution of carbon dioxide in the lungs must be increased, and its relative tension reduced in the region of the tissues. Current work tends to show more and more how exactly the chemical mechanisms of the blood are adjusted to give it the highest possible efficiency as a medium of gaseous exchange, and to indicate the great interest that the case of hæmoglobin presents to the physical chemist.

Many papers have appeared dealing with tissue respiration, especially in connexion with the nervous system. H. M. Vernon,[80] and, also, independently, F. Battelli and L. Stern,[81] have studied the depressing action of anæsthetics on the tissues oxydases, and their results have an important bearing on the nature of narcosis. F. G. Alexander and S. Cserna[82] find that the brain displays a considerable gaseous metabolism, its oxygen consumption being of the order of 0·36 c.c. per gram per minute. Narcosis depresses this metabolism greatly. The action of various narcotics differs, however, in detail, and any theory of anæsthesia must take account

[77] T. Lewis, J. H. Ryffel, C. G. L. Wolf, T. Cotton, G. L. Evans, and J. Barcroft, *Proc. physiol. Soc.*, 1913, liii–liv ; *J. Physiol.*, **46** ; *A.*, i, 1022.

[78] J. M. H. Campbell, C. E. Douglas, J. S. Haldane, and F. G. Hobson, *J. Physiol.*, 1913, **46**, 301 ; *A.*, i, 1011.

[79] J. Christiansen, C. G. Douglas, and J. S. Haldane, *Proc. physiol. Soc.*, 1913, ii ; *J. Physiol.*, **47** ; *A.*, i, 1403.

[80] *Biochem. Zeitsch.*, 1913, **47**, 374 ; *A.*, i, 220.

[81] *Ibid.*, 1913, **52**, 226, 253 ; *A.*, i, 929.

[82] *Ibid.*, 1913, **53**, 100 ; *A.*, i, 1011.

of such differences. S. Tashiro[83] claims to have measured the carbon dioxide output of nerve-fibres, which is also reduced by anæsthetics.

H. E. Roaf[84] has shown that during decerebrate rigidity the oxygen intake of the animal is only slightly greater than when the muscles are flaccid; whilst K. Hannemann[85] finds that removal of the brain markedly increases (in frogs) the total gaseous metabolism.

Miscellaneous Papers of Interest.

Functions of the Thyroid Gland.—Space has not allowed me to deal in a special section with the subject of internal secretions. I hope, however, to illustrate the work of the year in this domain by referring here to two interesting researches. The first throws light from a somewhat new experimental point of view on the importance of the thyroid gland as a regulator of the bodily functions. G. F. Mansfeld, in conjunction with Fr. Müller, has shown that the increased nitrogenous metabolism which is induced in normal animals by deficiency of oxygen does not occur in animals deprived of their thyroid gland. Other phenomena depending on the same deficiency are now shown by further work of the first-named author[86] to be absent when the gland is absent. Normal animals when kept at high altitudes are well known to develop a considerable increase in the number of red corpuscles in their blood. In Mansfeld's experiments (on rabbits) the control animals showed an increase of some 20 per cent. when removed from sea-level to a height of 1000 m. The phenomenon was wholly absent in the case of thyroidectomised animals, the blood of which reacted indeed in an opposite sense, and showed a large decrease of corpuscles. In the absence of the gland oxygen deficiency would seem actually to inhibit red cell formation. As a result of its removal the blood also regenerates more slowly and less completely after the administration of poisons which destroy red corpuscles. These results suggested an attempt to get an increase in corpuscles by injecting thyroid extracts into normal animals, and in Mansfeld's experiments the continued administration of such extracts did, as a matter of fact, cause an increase which in some cases amounted to 180 per cent.

Next it was shown (by Mansfeld and E. Hamburger) that the familiar rise in nitrogen excretion which occurs shortly before death from starvation was greatly reduced as the result of previous thyroidectomy. Finally, it was found that chloroform and kindred

[83] *Amer. J. Physiol.*, 1913, **32**, 107; *A.*, i, 930.
[84] *Quart. J. expt. Physiol.*, 1913, **6**, 393; *A.*, i, 1124.
[85] *Biochem. Zeitsch.*, 1913, **53**, 80; *A.*, i, 1011.
[86] *Pflüger's Archiv*, 1913, **152**, 23, 50, 56.

narcotics no longer induce an increased tissue breakdown when the gland is absent. These previously familiar effects of high altitudes, starvation and chloroform poisoning, are not, therefore, direct effects; they arise indirectly from the disturbance of thyroid function.

The Secretion of Cerebro-spinal Fluid.—W. E. Dixon and W. D. Halliburton[87] have now brought to a conclusion a lengthy and important research dealing with the cerebro-spinal fluid. The first paper, which is now published, deals with the secretion of that fluid. The process provides another instance of glandular activity controlled by chemical influences. The secretory mechanism is made up of the cubical epithelium cells which cover the choroid plexuses of the brain, called collectively, by Mott, the choroid gland. Dixon and Halliburton find that the stimulating hormone may be extracted from the gland tissue itself, but as extracts of the brain are equally effective the substance would seem to take its real origin from the metabolism of the latter organ. In cases of general paralysis and brain softening the hormone is found in the cerebro-spinal fluid itself, although not in the normal fluid. Carbon dioxide also acts in stimulating an increased flow, and the suggestion seems to be that the whole mechanism is adjusted to remove waste products, the flow of fluid being proportional to the metabolism in the brain.

The Secretion of Pancreatic Juice.—A fact of no small interest comes to light in a research due to A. Hustin.[88] If the isolated pancreas is perfused with oxygenated Locke's fluid, the gland remains long capable of secretion, but no secretion occurs. Addition of secretion to the fluid is quite without effect. When again the gland is perfused with blood alone, secretion of juice is also absent, but it becomes profuse when secretion is added to the blood. The juice so obtained is similar to that obtained from a fistula, containing all the normal ferments. The experiments of the author throw no very clear light on what constituent or constituents of the blood may be essential to the secretion. Serum containing secretion does not activate the gland, a fact which seems to militate against any simple assumption concerning the nature of the influence of the blood.

F. G. Hopkins.

[87] *J. Physiol.*, 1913, **47**, 215; *A.*, i, 1413.

[88] *Ann. et Bull. Soc. roy. de sc. méd. et nat. Bruxelles*, **70**, 178; from *Zentrbr. Bioch. ü. Biophysic*, xv, 83.

' AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

Whilst nothing of very exceptional importance has to be recorded for the year 1913, activity in research has been well maintained and much useful work has been accomplished, especially in connexion with soil chemistry and bacteriology. Many investigations, too, have been made which relate to the composition of different plants. These, however, deal as a rule with special cases, and cannot usefully be discussed as a whole.

Amongst publications which have appeared during the year may be mentioned "The Fertility of the Soil" by E. J. Russell, a second edition of E. A. Mitscherlich's "Bodenkunde," and a new "Journal of Agricultural Research," published by the United States Department of Agriculture, to take the place of the various bulletins hitherto issued by the different bureaus.

The Atmosphere.

The amount of combined nitrogen present in the atmosphere of different places, as indicated by the amounts brought down by the rain, and, as regards ammonia, the amounts absorbed by an acid solution of known area, has received a good deal of attention during the last few years. These recent results show that the average amount of nitrogen, in the forms of ammonia and nitric acid, which the rain contributes to the soil is rather less than four pounds per acre per annum, which agrees very nearly with the average amount found at Rothamsted during the last thirty years. The results obtained at different places vary, however, considerably. In Groningen the total nitrogen amounts to 2·6 kilos., whilst in New Zealand, near the coast, the amount is only 0·7 kilos. per acre. The greatest differences are in the nitrogen in the form of ammonia, which varies from 2·0 kilos. in Groningen to only 0·3 kilos. in New Zealand.

It is evident from all these results that as a source of combined nitrogen the rain is of no great importance to crops—an average yield of wheat or barley will contain eight times as much nitrogen. The question possesses interest, however, in its relation to the nitrogen of the soil, since we cannot yet say whether rain and dew,

apart from smoke contamination, are really supplying additional nitrogen to the soil, or merely restoring some of the ammonia previously lost.

Recent analyses of rain-water[1] obtained from the Outer Hebrides and from Iceland show that the air in the north of Lewis and in Iceland contains considerably less combined nitrogen than even the low amount found in New Zealand. At Vifilsotodum, Iceland, the total nitrogen only amounted to about 0·45 kilos. per acre per annum, mostly in the form of ammonia; whilst at the Butt of Lewis the total nitrogen is less than 0·35 kilos., the amounts of nitrogen in the two forms being about equal. These results, in conjunction with those obtained at other places near the sea, indicate that the sea, at any rate, does not contribute, as has been suggested, any very appreciable amount of ammonia to the air, even in tropical countries. So that, apart from local smoke contamination, it seems probable that atmospheric ammonia must be mainly derived from the soil. We have evidence that the fairly heavy soil at Rothamsted loses ammonia for some weeks after the application of ammonium salts, and it is possible that some soils are more or less continuously giving up to the air small portions of the ammonia produced from organic residues. Some soils may be expected to lose more ammonia than is returned in the rain, whilst others may gain in this manner more than they lose.

Chlorides and sulphates have also been estimated in numerous samples of rain collected in Russia,[2] and a large number of more comprehensive analyses of rain-water have been made in the neighbourhood of Leeds, in connexion with an investigation on the injury to vegetation caused by atmospheric impurities near an industrial town.[3] The results show that the amount of sulphur, which is mainly in the form of sulphates, is the most characteristic indication of the extent of contamination with coal smoke. At a distance of seven miles from the city the lowest amount of sulphur (as sulphur trioxide) was 58 kilos. per acre per annum, or about seven times the amount found at Rothamsted. On the other hand, the amounts of total nitrogen are not very high, being, at a distance of seven miles, only about 3 kilos. per acre, or, if some abnormally high results are excluded, a good deal less.

Soils.

Whilst much attention has been given to the mechanical and chemical composition, that is to say, the separation of soils into

[1] N. H. J. Miller, *J. Scot. Met. Soc.*, 1913, [iii], **16**, 141; *A.*, 1914, i, 128.

[2] P. Kossowitsch, *J. exper. Landw.*, 1913, **14**, 181; J. Wituynj, *ibid.*, 1911, **12**, 20; *A.*, 1911, ii, 432.

[3] C. Crowther and D. N. Steuart, *J. Agric. Sci.*, 1913, **5**, 391.

particles of different sizes, and the estimation of the various elements which they contain, the mineralogical composition which must influence both the physical and chemical properties of soils, has hitherto been rather neglected, notwithstanding recent improvements in methods, especially those dealing with the optical properties of minerals.

Recently a considerable amount of work has been done by the United States Bureau of Soils,[4] and the methods which have been found most suitable have been brought together and published, along with a description of soil-forming minerals. Although it is probable that all minerals occur sometimes, the great majority must be exceptional, so that the number of minerals to be looked for is comparatively limited. Minerals, such as leucite, which are readily decomposed would only be found near the places of their origin. The usual potassium minerals which occur in soils are muscovite, which is the most resistant, and probably of only slight value as a source of potassium for plants; biotite, which is the least resistant; orthoclase and microline. The common calcium minerals are epidote, which was found in most soils, hornblende, plagioclase, and garnet. The presence of quartz crystals probably indicates a limestone origin.

A study of the effects of frost on soil colloids[5] showed that in the case of soils which would be expected to be only slightly influenced, the soil particles become more finely divided, so that hygroscopicity is increased, whilst in the case of soils in which the colloids are appreciably coagulated by frost the hygroscopicity is diminished.

The cause of the plasticity of clay,[6] about which opinions have been very conflicting, has been shown to be due to the presence of organic aluminium compounds. A solution of humus, to which alumina was added in order to clarify it, on being filtered and evaporated, yielded a glue-like substance, which, when decomposed with hot concentrated hydrochloric acid, was found to contain aluminium.

Considerable further progress has been made in isolating the organic constituents of soils,[7] and the number of compounds found now amounts to thirty-five, including thirteen acids, nine bases, three sugars, two alcohols, and two aldehydes, besides a hydrocarbon, a glyceride, a resin ester, sulphur and phosphorus compounds, and an acid anhydride. Most of the remaining, still

[4] W. J. McCaughey and W. H. Fry, *U.S. Dept. Agric. Bureau of Soils Bull.* No. 91; McCaughey, *J. Ind. Eng. Chem.*, 1913, **5**, 562; *A.*, i, 1035.

[5] P. Ehrenberg and G. Freiherr von Romberg, *J. Landw.*, 1913, **61**, 73.

[6] J. Stewart, *Eighth Inter. Cong. Appl. Chem.*, 1912, XV, 266.

[7] E. C. Shorey, *U.S. Dept. Agric. Bureau of Soils Bull.* No. 88, 1913.

unexplored, portion of the organic matter is believed to consist mainly of resinous substances.

Owing to the rapid decomposition of the nucleic acids even by dilute mineral acids at the ordinary temperature, it is a difficult matter to distinguish between the organic and the inorganic phosphorus of soils, and impossible to distinguish quantitatively. When, however, the acid filtrate is immediately treated with sodium acetate and a large amount of alcohol, some of the nucleic acid can be recovered, and in this manner its presence has been detected in a number of soils. All of the organic phosphorus is probably in the form of substituted phosphoric acids. In organic sulphur compounds, on the other hand, the sulphur takes the place of oxygen, and when they are decomposed, sulphur, or a sulphide, is formed. The only sulphur compound so far isolated is trithiobenzaldehyde.

It must be borne in mind that whilst the organic substances which have been isolated are extracted from soils by dilute alkali, they do not form a part of the humus precipitate obtained by adding acid, which, after all, is the most interesting portion of the organic matter of soils, but are obtained from the filtrate from the humic acid.

During the last few years doubts have been expressed as to the existence of humic acids.[8] It is maintained that the action of peat on tricalcium phosphate, from which it liberates phosphoric acid, is not necessarily due to the presence of free acid in peat, and that it may be accounted for by the absorption of bases by colloids. Similarly, the action of peat in liberating iodine from a solution of potassium iodide and iodate is also attributed to the absorption of the base by colloids. As regards the inversion of sucrose by peat and the liberation of hydrogen when peat is boiled with water in presence of powdered iron, both these actions are attributed to the action of the hot water, assisted by the salts present in the peat.

The absorption of bases by peat colloids is attributed mainly to the cell-wall of the *Sphagnum*, so that according to this supposition the substances known as humic acid, which are precipitated by acids from alkaline extracts of peat or soils, are comparatively unimportant.

The question of the existence of humic acids seems now to be definitely settled[9] in favour of the old theory, which dates from the time of Sprengel, by a series of experiments made with the "*matière noire*" itself, instead of with peat, thus avoiding all

[8] E. Gully, *Mitt. k. Bayr. Moorkulturanst.*, 1913, Heft 5, 85; *A.*, i, 1353.

[9] P. Ehrenberg and F. Bahr, *J. Landw.*, 1913, **61**, 427; *A.*, 1914, i, 50.

complications due to the various other substances, whether colloids or not, present in peat. This, of course, is in any case desirable, and especially so when physical methods, such as conductivity measurements, have to be employed.

The crude ammonium humate employed in these experiments was prepared in the usual manner from peat. The solution was first filtered through collodion, which allows the humate to pass through fairly rapidly, whilst a colloidal substance is retained.[10] After concentrating the filtrate by evaporation at 55° under reduced pressure, the humic acid is precipitated with a small amount of hydrochloric acid, filtered through collodion, washed, and finally freed from electrolytes by means of a Zsigmondy dialyser. Humic acid prepared in this manner readily dissolves in alkali, even after it has been heated to 100° or 110°.

It was found, in the first place, that whilst ammonium humate has no definite dissociation pressure, its behaviour indicates that the ammonia is not merely adsorbed, but that it is held by the whole of the solid humic substance. The behaviour of the salt closely resembles that of ammonium guaiaconate, except that the latter gives up its ammonia very much more readily than the humate. This is in accordance with the view that humic acid is not merely a phenolic compound, but a true acid.

Further experiments on the absorption of ammonia and sulphur dioxide respectively showed that ammonia is absorbed in far greater quantity than sulphur dioxide, the former being chemically combined, whilst the latter is merely adsorbed.

The neutralisation point of humic acid was found by adding a suspension of the acid in water to dilute sodium hydroxide, and estimating the conductivity. The results indicated with sufficient clearness an equivalent weight of 230. It was further shown that the acid is probably tribasic, and, at any rate, not more than tetrabasic. So that the molecular weight of the acid would be either 690 or 920. It was not, however, found possible to prepare salts of definite composition. When calcium chloride is added to a solution of sodium humate, most of the humic acid is precipitated as calcium salt. The analysis of two different preparations gave, however, very low results for calcium; in one case about 20 per cent., and in the other nearly 30 per cent. lower than the theoretical amount. This accords with the idea that humates are solid solutions, and if this view is correct, the fact that a calcium salt has been obtained containing within 2 per cent. of the theoretical amount of calcium must be attributed to chance.

Pure humic acid was found to decompose about one-sixth of its

[10] S. Odén, *Ber.*, 1912, **45**, 651; *A.*, 1912, i, 336.

weight of tricalcium phosphate. Peat containing 5 or 6 per cent. of humic acid would, accordingly, liberate the phosphoric acid of about 1 per cent. of tricalcium phosphate.

The effects of the partial sterilisation of soils by moderate heating, and by various antiseptics, to which reference has been made in previous reports, have been further investigated,[11] and some additional evidence has been obtained that the beneficial results are due to the destruction of organisms which in some way hinder the multiplication of certain desirable bacteria. Briefly, the chief results are as follows: The immediate effect of heating soils to 55—60°, or of the application of antiseptics, is the destruction of the large organisms (protozoa, etc.) and of nitrifying organisms, whilst the organisms which produce ammonia, and denitrifying organisms, remain. Ammonia is at once produced, and goes on increasing in amount when the soils are kept. This is shown to be due to a rapid increase in the number of ammonifying organisms; there is no evidence that these organisms are in any way stimulated. The increase in numbers is still more marked when the conditions are rendered more favourable by increased temperature and by an increased supply of moisture. This is an important point, because all attempts to obtain a regular increase in the number of organisms by making the conditions of temperature and moisture more favourable have been unsuccessful when normal, unsterilised soils were employed. In normal soils the activity of the bacteria will, of course, be increased, but their numbers will be kept down, and at times even reduced, by the coincident increase in the number of large organisms.

The inoculation of partly sterilised soils with untreated soil restores the less favourable conditions, and again reduces the number of bacteria. In treated soils the increase in the number of ammonifying bacteria is sometimes accompanied by an increase of ammonia; in some cases ammonia production ceases, whilst the organisms continue to increase in numbers. The cessation of ammonia production, which may be brought about by adding ammonia, is due to a retarding action of ammonia on the activity, but not on the multiplication of the bacteria.

Finally, it is shown that soils are temporarily benefited in precisely the same manner by being kept for some time at a temperature of only 35°, and also by very low temperatures. The slow return of the soils, thus treated, to their original state supports the view that it is to the large organisms, rather than to the bacteria, that the beneficial effects of partial sterilisation must be due.

[11] E. J. Russell and H. B. Hutchinson, *J. Agric. Sci.*, 1913, **5**, 248.

Whatever slight physical or chemical changes soils may undergo when treated in the manner adopted in these experiments, it seems evident that they cannot in any way account for the results obtained, which seem clearly to point to the destruction of inimical organisms as the cause of the increased bacterial changes in the soils.

The way in which these large organisms check the multiplication of the bacteria is not yet evident. It is suggested that they feed on the bacteria; or that in some way they enclose, or lock up, the food on which the bacteria depend. It is perhaps more likely that their action consists in appropriating too large a share of the limited supply of oxygen in the soil. This, however, will, no doubt, be made clear by a better knowledge of the numbers and habits of the protozoa and other large organisms present in soils, and now being investigated.[12] In the meantime the results referred to constitute a distinct advance in our knowledge of the mutual relations of the different groups of soil organisms.

Antiseptics, such as arsenic compounds,[13] when applied to the soil in small amounts, seem to act similarly to volatile antiseptics, giving rise to increased ammonification and nitrification. Of the different arsenic compounds employed, lead arsenate was found to be the most stimulating and the least injurious, whilst Paris green proved to be the least stimulating and the most toxic. It was further shown that with fifty per million of arsenic, soluble in water, in the soil, both ammonification and nitrification can proceed vigorously It is not shown whether these results are due only to the destruction of large organisms, or whether there is, in addition, a stimulating action on the bacteria.

In connexion with the partial sterilisation of soils some interesting results have been obtained which throw light on the action of lime on soil organisms.[14] It has been shown that the increase in the number of bacteria, produced by the application of small amounts of lime,[15] is coincident with a destruction of the large organisms; and that lime, in the amounts employed, has an antiseptic action intermediate between the effects produced by heating and by volatile antiseptics respectively. The advantages of lime over volatile antiseptics are evident, since in addition to immediate antiseptic and chemical action, it leaves an essential constituent in the soil after its conversion into carbonate. The old practice of chalking will, in any case, have to be revived, sooner or later, and

[12] T. Goodey, *Proc. Roy. Soc.* 1913, B, **86**, 427.
[13] J. E. Greaves, *Biochem. Bull.*, 1913, **3**, 1.
[14] H. B. Hutchinson, *J. Agric. Sci.*, 1913, **5**, 320.
[15] H. Fischer, *Landw. Versuchs-Stat.*, 1909, **70**, 335 ; *A.*, 1909, i, 602.

if lime should prove to be a suitable antiseptic under practical conditions it could easily be applied, at suitable intervals, or alternately with chalk.

Vegetation experiments in which 0·5 per cent. of lime was added to arable soil, already containing calcium carbonate, showed a remarkable increase. With rich garden soil the first crop was depressed, and the benefit of lime was only shown by the second crop, which was increased very considerably. The temporary injury in the case of garden soil is probably similar to what has been observed with peaty soils. It has been attributed, on the one hand, to increased oxidation of organic matter and the production of toxic substances,[16] such as oxalic acid (which, as time goes on, would be converted into carbonates); and, on the other hand, to a reduction of nitrates to nitrites in amounts sufficient to be toxic.[17]

The chemical effects of heating soils to higher temperatures, such as 135° and 150°, have also been investigated. At the lower temperature[18] it was found that not only ammonia and amines are liberated, but that there is an increase in all the water-soluble substances, and an increase in acidity. Arginine, xanthine, hypoxanthine, guanine, cytosine, and dihydroxystearic acid are formed, or, if already present, their amounts are increased. Whilst both beneficial and injurious substances are produced, the latter have a predominating effect, and must be got rid of before the benefits of heating can become evident.

Soils which were heated to 150°[19] and dialysed were found to contain much more soluble matter than before, and vegetation experiments showed that more growth was obtained, and more mineral matter assimilated in the heated soil. Similar results, although less marked, were obtained by drying the soil at 95—98° in a vacuum. Increased assimilation of mineral matter (potassium and phosphorus) was also observed in the case of tomatoes grown in partly sterilised soil which had been dunged.[20] In this case the

[16] G. A. Ritter, *Bied. Zentr.*, 1913, **42**, 239; *A.*, i, 812.

[17] A. Densch, *Landw. Jahrb.*, 1913, **44**, 331.

[18] O. Schreiner and E. C. Lathrop, *U.S. Dept. Agric. Bureau of Soils Bull.* 89, 1912; Lathrop, *Eighth Inter. Cong. Appl. Chem.*, XV, 147; *A.*, i, 1036. The authors' statement that changes in soils brought about by the action of heat were first observed by Frank in 1888 is not quite correct. Warington previously showed that aqueous extracts of heated soils contain greatly increased amounts of organic matter (*T.*, 1883, **41**, 356), and that nitrates can be completely destroyed when soils are heated in a moist condition (*ibid.*, 354). Pitsch (*Landw. Versuchs-Stat.*, 1887, **34**, 217) showed that ammonia is produced when soils are heated.

[19] J. König, J. Hasenbäumer, and K. Glenk, *Landw. Versuchs-Stat.*, 1913, **79–80**, 491; *A.*, i, 578.

[20] E. J. Russell and F. R. Petherbridge, *J. Agric. Sci.*, 1913, **5**, 248.

soil was only heated to 55° and 98°, or treated with volatile antiseptics.

In connexion with the question of the losses of ammonia from soils, a number of experiments have been made, in which different kinds of soils, to which solutions of ammonium carbonate were added, were kept in closed vessels through which a rapid current of air was passed, and the amount of ammonia which was given off was estimated.[21] The results obtained when soil and ammonium carbonate alone were employed accorded with what would be expected from the characters of the soils. That is to say, the soils containing a good deal of humus and clay retained the greatest amount of ammonia. When, however, calcium carbonate was added, different results were obtained in each case. The absorptive power of the most retentive soil, which contained the greatest amount of organic matter and clay, and was also the most acid, was diminished by the presence of calcium carbonate, and a similar result was obtained with the least retentive soil, which was only slightly acid, and contained less than 1 per cent. of organic matter and less than 4 per cent. of clay. On the other hand, two other soils, the one very similar to the last-mentioned, and the other containing a fair amount of humus and more clay, were both benefited, as regards absorptive power, by addition of calcium carbonate. Further experiments showed that the effect of calcium carbonate may not only be quite different with different soils, but that it is also influenced by the amount of ammonium carbonate present. Those soils in which calcium carbonate increased the loss of ammonia when small amounts of ammonium carbonate were applied, diminished the losses when larger amounts were present. The increased absorptive power in presence of calcium carbonate is attributed to the production of calcium zeolites. Whether a favourable effect will be obtained when small amounts of ammonium carbonate are present, or only with larger amounts, seems to depend on the amount of available potassium which the soil contains.

Ammonification, Nitrification, and Denitrification.

A new denitrifying organism, *Denitrobacterium thermophilum*, has been obtained from soil which produces vigorous growth at 60—65°, and decomposes nitrates, with liberation of nitrogen, both from the nitrates and from the nitrogenous matter of the broth. The nitrogen of nitrates is partly converted into oxides of nitrogen.[22]

[21] O. Lemmermann and L. Fresenius, *Landw. Jahrb.*, 1913, **45**, 127.

[22] A. Ambrož, *Centr. Bakt. Par.*, 1913, ii, **37**, 3 ; *A.*, i, 568.

A comparison of the results obtained in ammonification experiments in soil and in solutions indicated that the more useful indications are obtained in solutions.[23] In experiments in solutions, under aerobic conditions, the amount of substance employed seems to be without influence on the rate of ammonification. Under anaerobic conditions ammonification is retarded owing perhaps to an accumulation of injurious metabolic products. Whilst in the initial stages of the process, in shallow layers of liquids, it seems possible that aerobic and anaerobic organisms may be of equal importance, it is considered that aerobic organisms may predominate more in the final stages of ammonification. Blood and horn meal decompose more rapidly in soil than in solutions, except when deep layers of soil are compared with shallow layers of solution. Aeration would therefore seem to be one of the chief conditions on which ammonification depends.

An interesting series of experiments has been described on the ammonification of dried blood in soils, as effected by antagonism between anions.[24] Soil to which 2 per cent. of dried blood and the optimum amount of water were added, together with some salt in sufficient quantity to be toxic and varying amounts of some other salt, were kept at 28—30° for four days, and the amount of ammonia which was produced estimated. It was found that antagonism, as indicated by its effects on ammonification, exists between sodium chloride and sodium sulphate, between sodium chloride and carbonate, and between sodium sulphate and carbonate. The strongest antagonism is between sodium carbonate and chloride; the weakest between sodium chloride and sodium sulphate. When the actual amounts are considered, the greatest antagonism was observed when the soil contained 0·2 per cent. of sodium chloride and 0·7 per cent. of sodium carbonate. Under the latter conditions 70·7 milligrams of nitrogen as ammonia was obtained, whilst with decreasing amounts of sodium carbonate the amount of nitrogen as ammonia fell rapidly to 37·8 milligrams with 0·2 per cent.

The results are of considerable interest, both theoretical and practical, and suggest possibilities in reclaiming the large areas of "alkali" soils. The methods of flooding and draining such soils is not only costly but wasteful, since the water carries away plant food along with the toxic salts. The difficulty may possibly be overcome by selecting plants which resist the action of the alkali, and aiding them by the application of suitable amounts of salts which are antagonistic to those already present.

The recent observations, in Colorado, of great accumulations of

[23] F. Löhnis and H. H. Green, *Centr. Bakt. Par.*, 1913, ii, **37**, 534 ; *A.*, i, 797.
[24] C. B. Lipman, *ibid.*, 1913, ii, **36**, 382 ; *A.*, i, 238.

nitrates in certain alkali soils—so great as to cause the destruction of trees—seems now to be satisfactorily accounted for without assuming the intervention of abnormally active nitrogen-fixing and nitrifying organisms. As regards nitrification, the results of experiments with arid soils in Utah [25] showed that, with suitable addition of water, nitrification was considerably less active than in Rothamsted soils.

In arid soils the nitrates are invariably accompanied by other salts, such as calcium, sodium, and magnesium chlorides and sulphates; and as an examination of the results obtained in Colorado shows that the amounts of chlorides rise and fall with the nitrates, it may be safely assumed that the nitrates and the chlorides have a common origin, both being derived from accumulations in the subsoil, deposited in remote times.

It has been observed that a year or so before alkali soils became sterile, luxuriant crops are obtained owing to an upward movement of nitrates. Later on the salts become so concentrated that the plants are killed.

The large yields obtained on arid soils, notwithstanding the small amount of organic nitrogen they contain, has been attributed to the fact that the humus is more nitrogenous than in humid soils. It is, however, considered more probable that the fertility is due to the deposits of nitrates. It is sometimes found that owing to the nitrates of the subsoil being taken up by deep-rooted plants, and the ploughing in of the straw, the surface soil of cultivated arid land becomes richer in organic matter than the adjacent, uncultivated soils.

In the course of an investigation on the amounts of nitrates in Rothamsted soils about thirty years ago it was shown that, under otherwise similar conditions, soils and subsoils down to a depth of nine feet contained very much more nitrogen as nitrates where a leguminous crop had been grown than with a gramineous crop. The conclusion was drawn that the growth and the crop-residues of leguminous plants were more favourable to the development of nitrifying organisms than that of gramineous plants.[26]

Recent experiments on nitrification in surface soils taken from fields on which lucerne and timothy had been grown showed that nitrification was more rapid in lucerne soil than in timothy soil, not only in the case of soils on which the crops had been grown continuously, but on soils which had been left fallow for two years.[27] The greater production of nitrates in the lucerne soil was

[25] R. Stewart, *Centr. Bakt. Par.*, 1913, ii, **37**, 477.
[26] J. B. Lawes and J. H. Gilbert, *T.*, 1885, **47**, 380.
[27] T. L. Lyon and J. A. Bizzell, *Centr. Bakt. Par.*, 1913, ii, **37**, 161.

not due to the presence of a more highly nitrogenous crop residue, because the rate of nitrification remained in the same order when both soils contained about the same amounts of nitrogen in the form of dried blood. Whilst addition of lime considerably increased the amounts of nitrates formed, the leguminous soil still showed an excess over the timothy soil. In what way nitrification is promoted by the growth of a leguminous crop remains to be ascertained.

As regards the numbers of bacteria, without reference to the kinds, present at different depths of the same soil under different crops, and in different kinds of soils,[28] a good deal depends on the mechanical composition, and consequently the aeration. The greatest number occurs in the upper four inches, below which there is a more or less gradual decrease in numbers down to five feet. In one case samples were taken down to fifteen feet; at that depth the soil contained about 250 bacteria per gram. Considerable numbers of bacteria were found at much lower depths in loess soil than in drift soil. The greatest fall in numbers, from the surface downwards, occurred within the first eight or ten inches. When the surface soils of different kinds are compared it is seen that loess soil contains the largest number of bacteria, and woodland soil the fewest. The latter result accords with previous investigations.

The most interesting of the results are those relating to different areas of the same soil under various crops. It was found that a rotation of crops increased the number of bacteria as compared with continuous cropping; and that in the top depth of four inches there were more bacteria with a three-year than with a two-year rotation. On the other hand, with a four-year rotation the numbers were lower than those of any plots except those under continuous clover and maize, and a two-year rotation in which rye was ploughed in. With continuous clover there were fewer bacteria in the top four inches than with continuous maize; at lower depths the differences were only slight.

Whilst it cannot be said that these results in any way support the ones previously referred to, they are not necessarily opposed, because here the bacteria as a whole are dealt with. The one series of experiments deals with the activity of one group of bacteria; the other with the numbers of bacteria generally.

The variations in the numbers of bacteria cannot be accounted for by variations in the moisture and in the amounts of nitrogen present, both of which were estimated in each case. It is suggested that aeration may be the chief factor, or that toxic substances are

[28] P. E. Brown, *Centr. Bakt. Par.*, 1913, ii, **37**, 497.

produced by the plants. The former explanation seems to be the more probable—until toxins have been detected.

A biological investigation of different kinds of peat in Denmark,[29] the one a raw peat covered with heather and containing 1 to 1·5 per cent. of nitrogen, the other from more humified peat land, employed for grazing, which contained about 3 per cent. of nitrogen, showed very considerable differences in bacterial activity. The heather peat ("Hochmoor") was found to possess comparatively high denitrifying power, whilst the putrefactive and mannitol decomposing bacteria showed only slight activity, and the cellulose decomposing bacteria extremely slight activity. Nitrifying organisms were not found. The grass peat, on the other hand, induced vigorous denitrification, nitrification, decomposition of peptone and mannitol, and a feeble decomposition of cellulose.

As regards the production of ammonia from the amino-acids present in soils, a series of experiments was undertaken to ascertain the relative rate at which ammonia is formed, and also whether the conversion into ammonia is quantitative.[30] Known amounts of the various compounds were intimately mixed with definite amounts of soil, and the ammonia estimated after keeping the mixtures for some days at 22—27° in closed vessels. The highest amount of ammonia was obtained from glycine (81·03 per cent.); asparagine gave 77·47 per cent., alanine 75·58, aspartic acid 72·74, glutamic acid 72·19 per cent., whilst tyrosine, leucine, and phenylalanine gave respectively 59·65, 59·62, and 54·31 per cent.

Whether the whole of the nitrogen of amino-acids can be converted into ammonia remains uncertain; some of the ammonia may be nitrified. It is, however, evident that these compounds readily lose nitrogen in the form of ammonia, and that the rate of ammonification is influenced by the constitution of the different compounds.

The ammonification of organic nitrogen seems to be retarded in solutions which are subjected to the influence of β- and γ-rays[31]; the activity of denitrifying organisms was also found to be considerably diminished, whilst the development of the bacteria was not affected.

Fixation of elementary nitrogen by *Azotobacter Chroococcum* was found to be distinctly increased when the air was activated by pitchblende, somewhat better results being obtained with weak than with stronger radioactive intensity.

[29] H. R. Christensen, *Centr. Bakt. Par.*, 1913, ii, **37**, 414.
[30] S. L. Jodidi, *Eighth Inter. Cong. Appl. Chem.*, 1912, XXVI, 119; *A.*, i, 1036.
[31] J. Stoklasa, *Compt. rend.*, 1913, **157**, 879; *A.*, i, 1421.

Plant Nutrition.

In a previous report (1910) reference was made to the theory that the fertility of a soil depends mainly on the capacity of the soil to supply adequate amounts of water to the crop, and that the action of manures consists not in supplying plant food, but in precipitating toxins secreted by the plant.[32] There seems to be some doubt as to whether the publication in which this theory appeared was intended to be taken quite literally, or whether it was not, in part, a rather drastic way of discouraging the purchase of the more useless mixed manures offered to unwary agriculturists. However that may be, one result is an important and interesting investigation,[33] which re-establishes the position of manures as essential in the nutrition of plants, and at the same time throws light on other conditions which affect the development of roots.

In the first place, water culture experiments were made with wheat and barley in which the plants were grown in extracts of soil from some of the differently manured plots of the permanent wheat and barley fields at Rothamsted; the solutions each received the same amount of nitrogen in the form of sodium nitrate, whilst as regards ash constituents the plants depended on the amounts extracted from the differently manured soils. Carefully selected seed was employed, and each unit consisted of ten plants, each in a separate solution, which were renewed at intervals of two weeks. Both plants were grown in extracts of soils from both fields. The results of the culture experiments not only showed differences in the different extracts, but the differences were very similar to those in the growth of the crops on the plots themselves. To complete the evidence, analyses of the extracts were made, in which both the total and citric acid soluble phosphoric acid and potassium were estimated. Whilst extracts of soil from plots which received no phosphoric acid contained from 0·525 to 0·881 per million of phosphoric acid, the ones derived from the manured plots contained about 4 per million. The potassium results were similar.

The experiments were repeated (with barley soils) so as to include, besides the soil extracts, an artificial culture solution of the same strength as the extracts from the completely manured plots; and soil solutions from partly manured plots with their deficiencies in essential constituents made good by adding phosphoric acid, or potash, or both. The conclusions drawn from the

[32] Whitney and Cameron, *Bull.* 22, 1903, *Bureau of Soils, U.S. Dept. Agric.*

[33] A. D. Hall, W. E. Brenchley, and L. M. Underwood, *Phil. Trans.*, 1913, B, 204, 179; *A.*, 1914, i, 126.

results of the first series were confirmed by the later experiments, and these showed, in addition, that the soil extracts, especially those from the dunged plots, were better media for plant growth than the artificial solutions; and it is suggested that this may be due to the presence of nitrogenous compounds which are utilised by the plants in the early stages of growth.

As regards the theory that plants secrete toxins which are unfavourable to the growth of succeeding crops of the same kind, it was found that both wheat and barley gave almost identical results whether grown in extracts of wheat or barley soils; both plants were slightly heavier when grown in solutions from barley soil than in solutions from wheat soil. Boiling the soil extracts, which should destroy any toxins, had no effect on the results; whilst evaporating the extracts to dryness, igniting, and redissolving the residue generally depressed the yields. The results seem conclusive against the toxin theory, especially when it is remembered that wheat had been grown continuously on Broadbalk Field for seventy years. (Toxins appear to occupy, in relation to plant chemistry, a position somewhat similar to colloids in soils, both being found useful in explaining otherwise difficult questions; except that whilst the colloids are there, the presence of toxins frequently has to be assumed.)

In order to ascertain the effects of varying concentrations of nutritive solutions, which has generally been assumed to be of no importance, at any rate within very wide limits, experiments were next made in which barley was grown in solutions containing 0·5 gram of potassium dihydrogen phosphate; magnesium and potassium sulphates and sodium chloride, 1 gram of potassium nitrate, and 0·04 gram of ferric chloride per litre, and in the same solutions diluted to 1/3, 1/10, and 1/20 respectively. From the commencement the amount of growth varied with the concentration of the nutritive solution, the final dry weight in the strongest solution being about six times as much as in the most dilute solution. Similar results were obtained when the plants were grown in coarse sand through which large amounts of the nutritive solutions were allowed to percolate, so as to ensure adequate amounts of plant food being available. It is evident, therefore, that apart from the total amount of available plant food, the concentration has a very marked effect on the rate of growth.

A further question arises whether plants growing in soil can obtain their food continuously, or whether, after the roots have exhausted the soil solution in their immediate neighbourhood, they have to wait for fresh food materials to diffuse. Barley plants were, accordingly, grown in silver sand containing 20 per cent. of nutri-

tive solution, in which condition it contained no free water, and could be crumbled readily. It was found that, compared with plants grown in solutions of the same strengths, there was not only no retardation of growth in the sand, due to slow diffusion, but that there was far more growth in sand than in water. Similar results were obtained when the nutritive solutions were supplied in porous cylinders which were placed in the sand in which the plants were growing, so that in this case the plant food had to pass through the walls of the cylinders before even reaching the sand.

A comparison of the growth obtained in various solid media with water cultures showed in each case a higher yield in the former. Coarse sand gave the best results, then kaolin, silt, and fine sand in the order as given. The roots only developed well in coarse sand and kaolin, being very restricted in fine sand and silt. As these results seemed to point to deficient aeration, more water culture experiments were made, in which some were not aerated whilst others were aerated daily or continuously. The effect of continuous aeration was to nearly double the amount of growth, and sufficiently accounts for the greater yields obtained in sand cultures as compared with solutions.

Taken altogether, these results show clearly that the composition of natural soil solutions is by no means constant but varies according to the manures applied. Also that the growth of crops depends, not merely on the amounts of plant food, but, within wide limits, on the concentration of the solution. And that the continuous growth of the same crop for sixty or seventy years does not leave behind a specific toxin having an injurious effect on the same or other crops.

Assimilation of Nitrogen Compounds.

Whilst the question of the direct assimilation of ammonium salts by plants may now be considered to be decided beyond doubt, a good deal remains to be done in connexion with the behaviour of different plants towards ammonium salts and the effect of these compounds as compared with nitrates. Not merely the final weights of the produce have to be considered, but also the rate of growth, and the effects of the different forms of nitrogen on the relative amounts of seed, leaf, and roots. It has been found in sand-culture experiments with mustard and wheat, under conditions of sterilisation,[34] that the greatest amount of leaf was obtained when sodium nitrate was employed as source of nitrogen, whilst ammonium salts gave the greatest amount of seed. Then, again,

[34] E. Pantanelli and G. Severini, *Biol. Zentr.*, 1913, **42**, 98; *A.*, i, 435.

as regards the behaviour of different plants, it is shown that mustard developed most quickly under the influence of sodium nitrate, whilst ammonium salts, especially of organic acids, gave better results with wheat than sodium nitrate.

In another series of cultures with peas and maize, also under sterilised conditions,[35] the plants received ammonium nitrate. It was found that the salt was not assimilated as a whole, but that the base and the acid were taken up in different proportions at different stages of growth. During the early stages of growth more nitrogen was assimilated in the form of ammonia than as nitrate, in the late period more nitrate than ammonia, whilst during the intermediate period ammonia and nitrate were taken up in about equal proportions. These results seem to accord with those of an old experiment with rice, in which it was found that the plants preferred ammonium salts at the commencement, and nitrates during later growth.[36] Whilst other ammonium salts are physiologically acid, ammonium nitrate is, according to these results, successively acid, neutral, and alkaline.

Some experiments made with etiolated seedlings showed very great differences in the behaviour of different groups of plants towards ammonium salts.[37] Certain plants, such as barley and maize, were found to absorb ammonia readily from dilute solutions of ammonium chloride and sulphate. Although addition of calcium carbonate is beneficial, it is not essential, and even without such addition, asparagine is readily formed from the ammonia supplied. With peas and vetches it was found that, in absence of calcium carbonate, salts of ammonium have a retarding effect on the decomposition of proteins and the production. Addition of calcium carbonate induced, however, an energetic absorption of ammonia and production of asparagine. In the case of lupines, the presence of ammonium salts seems to give rise to fundamental disturbances in the synthetic processes, even when calcium carbonate is present.

The different behaviour of peas and lupines towards ammonium salts is of considerable interest when it is remembered that both plants will grow luxuriantly when the only combined nitrogen at their disposal is that provided in their root-nodules by *Bacillus radicicola*. The fact that the two plants belong to different groups, each requiring its own modification for inoculation, would hardly seem to justify the conclusion that each modification makes use of a different process in assimilating elementary nitrogen. So that, on the supposition that all leguminous plants obtain the same

[35] J. Schulov, *Ber. Deut. bot. Ges.*, 1913, **31**, 97 ; *A.*, i, 688.
[36] O. Kellner and J. Sawano, *Landw. Versuchs-Stat.*, 1884, **30**, 18.
[37] D. Prianischnikov, *Rev. Gén. Bot.*, 1913, **25**, 5.

nitrogenous compound from their nodules, the compound is apparently not ammonia.

As regards the assimilation of nitrites, it has been found[38] that when potassium nitrite is dissolved in formaldehyde or in methyl alcohol and exposed to light, the solution contains methylamine, formic and hyponitrous acids, and hydroxylamine, whilst an alkaloidal compound containing a pyrrole ring is formed. As regards the view that nitroxyl, NOH, plays an important part in nitrogen assimilation, experiments on the action of mercury light on nitrites showed that liberation of oxygen is considerably accelerated by carbon dioxide, whilst substances of the nature of α-amino-acids were obtained from potassium nitrite and carbon dioxide, with ferric chloride as catalyst.

In connexion with the investigation on the soluble nitrogen compounds present in soils,[39] a number of water-culture experiments have been made in order to throw light on the behaviour of the various substances towards plants. It was found that wheat plants are benefited by argenine, asparagine, choline, creatine, creatinine, betaine, glycine, guanine, histidine, hypoxanthine, leucine, nucleic acid, phytine, and xanthine. Alanine, alloxan, and arbutin were also favourable to growth when sufficiently diluted, whilst benzidine, guanidine, α-naphthylamine, neurine, picoline, piperidine, pyridine, quinoline, scatole, solanine, and tyrosine were all found to be toxic.

Both histidine and argenine can take the place of nitrate, and when employed in conjunction with a nitrate, considerably less nitrate is assimilated than when employed alone.[40]

Glucosamine hydrochloride, which might be expected to be very suitable as a source of nitrogen, is shown to be toxic, at any rate to maize and beans. In the case of beans the substance was added to the solution in amounts from 50 mg. upwards per litre, and in every case caused the plants to wither.[41]

It is evident that the different nitrogen compounds which plants can utilise are far from being equally suitable; it has been found that when two or three compounds, such as histidine, creatinine, and asparagine, are supplied simultaneously, more nitrogen is assimilated than when each one is employed singly.[42]

[38] O. Baudisch and E. Mayer, *Ber.*, 1913, **46**, 115; *A.*, i, 324; and Baudisch, *Zeitsch. angew. Chem.*, 1913, **26**, 612; *A.*, i, 1424.

[39] O. Schreiner and J. J. Skinner, *U.S. Dept. Agric. Bureau of Soils, Bull.* 87, 1912.

[40] J. J. Skinner, *Eighth Inter. Cong. Appl. Chem.*, 1912, XXV, 253.

[41] M. L. Hamlin, *J. Amer. Chem. Soc.*, 1913, **35**, 1046; *A.*, i, 1142.

[42] O. Schreiner, *Eighth Inter. Cong. App. Chem.*, 1912, XV, 231; *A.*, i, 1143.

Plant Stimulants and Manure.

Whilst a considerable amount of attention continues to be given to the stimulation of plants by small amounts of metallic compounds, a good deal of the evidence is conflicting, owing, no doubt, to imperfect methods. The opinion has been expressed that most poisonous substances will act as stimulants in certain states of dilution; as, however, it would be hardly possible in practice to maintain the desired degree of dilution, and a comparatively small change may convert the stimulant into an active poison, the application of such compounds, even if their stimulating effect were to be satisfactorily proved, is not likely to be adopted.

In pot experiments with rice [43] it was found that sodium borate, manganese sulphate, ferrous sulphate, and zinc sulphate had favourable effects in 1/1000 mol. solutions, whilst copper sulphate, nickel sulphate, and cobalt nitrate were beneficial only when applied in 1/2000, 1/5000, and 1/10,000 mol. solutions. As the rice was grown in soil the concentrations are considered to be higher than they would be in water cultures. It is probable that in water cultures the results would have been quite different, as it has been shown that barley is not stimulated by copper sulphate in cultures containing 0·1 per million.[44]

Different plants are affected in different degrees by stimulating substances. Vines, for instance, were found to be stimulated by 0·001 per cent. solutions of manganese sulphate, and injured by higher concentrations. Garden beans showed greater stimulation than vines, and were also found to be better able to resist the action of stronger solutions.[45] In other experiments on germination [46] it was found that whilst uranium, copper, zinc, aluminium, and cadmium oxides hinder the germination of beans, maize is stimulated.

Uranyl nitrate, when applied to *Melilotus albus*, grown in pots, was found to be beneficial, especially when applied at the rate of 2·5 kilos. per hectare; whilst no toxic effect was observed when eight times this amount was employed. Lead nitrate gave similar results with oats and with buckwheat, but as little as 8 kilos. per hectare has a toxic effect.[47]

Boron [48] seems to be rather uncertain in its action on beans, and small amounts (1 per million as borax, or less when boric acid is

[43] M. Rocas, *Bied. Zentr.*, 1913, **42**, 41; *A.*, i, 235.
[44] W. E. Brenchley, *Ann. Bot.*, 1910, **24**, 571; A., 1910, ii, 889.
[45] L. Montemartini, *Bied. Zentr.*, 1913, **42**, 65; *A.*, i, 234.
[46] U. Varvaro, *Chem. Zentr.*, 1913, i, 546; *A.*, i, 570.
[47] J. Stoklasa, *Compt. rend.*, 1913, **156**, 153; *A.*, i, 324.
[48] E. Haselhoff, *Landw. Versuchs.-Stat.*, 1913, **79–80**, 399; *A.*, i, 429.

employed) acted favourably on the growth of the plants, whilst the appearance of the leaves indicated some injurious effect as well. In soil cultures 0·1 per million seemed to have a stimulating action; the results vary, however, with different plants.

Cerium and lanthanum carbonates,[49] in very small amounts, are found to be favourable to the growth of hyacinths, lanthanum carbonate having a special effect in lengthening the flower stalks. Unsatisfactory results were obtained with yttrium.

The results of pot experiments at Woburn [50] showed that lithium salts, applied at the rate of 20 per million, or less, to wheat growing in sandy soil, have a stimulating effect which seems to be exerted chiefly during the germinating period. Larger amounts of lithium (30 per million or more) are toxic. Comparing the different salts of lithium, it was found that the nitrate is the most active as a stimulant and also the most toxic.

Zinc salts also had a stimulating effect on wheat, and were toxic only when the amount applied reached 200 per million. Similar results were obtained with lead salts, which considerably increased the yield of grain and straw. The amounts employed were 100 to 300 per million, no toxic effect being observed with the highest amount.

In France a number of field experiments have been made, in which zinc and manganese salts were applied to different crops. With zinc sulphate (from 1 to 10 kilos. per hectare) the yield of maize was increased, whilst the results obtained with oats, rye, clover, and peas were irregular.[51] More striking results were obtained with manganese sulphate,[52] which increased the yield of peas 20 per cent., of colza 18 per cent., and of clover 15 per cent. As regards the amounts of manganous sulphate employed, the best results were obtained with from 30 to 50 kilos. of the anhydrous salt per hectare. The number of successful results obtained with manganese make it desirable that manganese should be more systematically looked for and estimated in soils and in plant ashes, than has been done hitherto.

Aluminium sulphate [53] applied to barley, grown in pots, at the rate of 2 per million, increased the yield of dry matter 17 per cent. Larger amounts (4 per million) failed to increase the dry produce, but increased the amount of water retained by the plants.

With reference to Loew's hypothesis that lime and magnesia have

[49] W. H. Evans, *Biochem. J.*, 1913, **7**, 349; *A.*, i, 1032.
[50] J. A Voelcker, *J. Roy. Agric. Soc.*, 1912, **73**, 314; *A.*, i, 1430.
[51] M. Javillier, *Bied. Zentr.*, 1913, **42**, 215; *A.*, i, 692.
[52] G. Bertrand, *ibid.*, 215; *A.*, i, 692.
[53] G. Bertrand and H. Agulhon, *ibid.*; *A.*, i, 692.

to be applied in definite proportions in order to obtain the best results, experiments at Woburn[54] showed that wheat is benefited by adding magnesia to soil in which it is deficient, provided that the amount does not exceed that of the lime. Whilst an excess of magnesia over lime has a toxic effect and diminishes the yield, lime in excess is not toxic.

Magnesia and lime are both capable of modifying the growth of wheat, and altering the character of the root and the composition of the grain.

Other experiments have been made, in which beans were grown for three years on small plots,[55] the soil of which contained lime and magnesia in different proportions. The results showed that on soils employed, the relation of lime to magnesia was without effect on beans, and that with increasing amounts of lime in the soil the percentage of lime in the plants remained the same. From these results the conclusion is drawn that whilst the ratio of lime and magnesia, and of other salts, sometimes affects the growth of plants, the hypothesis cannot be considered as applying to all soils. Results similar to these have also been obtained with a variety of plants grown in different soils.[56]

As regards the effect of sugar on crops, the results of pot experiments in which sugar was applied to a loamy sand, in conjunction with sodium nitrate and ammonium sulphate, showed that the yield of the first crop was depressed, whilst the second crop was increased. The final result showed no increase. It would seem that the low yield of the first crop was due to a portion of the nitrogenous manure being converted into proteins under the influence of the carbohydrate, and that the proteins were broken down in time for the second crop.[57]

Results similar to these were obtained in experiments on plots,[58] the yield being diminished the first year, increased the second year, whilst in the third year the application of sugar had no effect.

Ammonium sulphite applied as manure[59] varies in its effects according to the soil, and presumably the rate with which it is converted into sulphate, since in water cultures it proved to be very injurious. In a loamy soil it had the same effect as ammonium sulphate, in sand its action was somewhat less favourable, whilst in peaty soil the yield was much less than with sulphate. Calcium sulphite is somewhat toxic in water cultures and perhaps in peaty

[54] J. A. Voelcker, *J. Roy. Agric. Soc.*, 1912, **73**, 325; *A.*, i, 1429.
[55] P. L. Gile and C. N. Ageton, *J. Ind. Eng. Chem.*, 1913, **5**, 564; *A.*, i, 1034.
[56] E. Haselhoff, *Landw. Jahrb.*, 1913, **45**, 609.
[57] M. Gerlach and A. Densch, *Bied. Zentr.*, 1913, **42**, 21.
[58] T. Pfeiffer and E. Blanck, *Landw. Versuchs.-Stat.*, 1912, **78**, 375.
[59] W. Thalau, *ibid.*, 1913, **82**, 161; *A.*, i, 1029.

soil, whilst no injurious effect was noticed in loamy and sandy soils. Sodium thiosulphate also produced no injurious results.

In an experiment with sugar beet[60] the application of sulphur was found to increase the yield slightly, but was without influence on the amount of sugar and the quality of the juice.

The manurial value of cyanamide has been shown by the results of pot experiments with oats to be increased by the addition of molasses and by ferric oxide. The effect of molasses is attributed to increased production of carbon dioxide in the soil, whilst ferric oxide accelerates the production of carbamide. The ferric oxide can be applied in the form of bog ore at the rate of 50 kilos. per hectare.[61]

Methods.

From the earliest days of agricultural chemistry to the present time the inadequacy of methods of analysis has always been a source of difficulty.

Amongst new methods published during the year, reference may be made to a paper of considerable importance on the estimations of carbohydrates, with special reference to plant extracts.[62]

For the estimation of carbonates in soils, a method has been devised in which the carbon dioxide is liberated by means of cold dilute phosphoric acid, which has very little action on the organic matter. A current of air, slow at first and rapid afterwards, is passed through the apparatus for half-an-hour, and the carbon dioxide estimated gravimetrically or volumetrically.[63]

N. H. J. Miller.

[60] J. Urban, *Zeitsch. Zuckerind. Böhm.*, 1913, **37**, 441 ; *A.*, i, 810.

[61] A. Stutzer, *Eighth Inter. Cong. Appl. Chem.*, 1912, XV, 9 ; *A.*, i, 1144.

[62] W. A. Davis and A. J. Daish, *J. Agric. Sci.*, 1913, **5**, 437 ; this vol., p. 186.

[63] W. H. MacIntyre and L. G. Willis, *Agric. Exper. Stat. Univ. Tennessee Bull.*, 100, 1913.

MINERALOGICAL CHEMISTRY.

Numerous lines of crystallographic inquiry all converge to the conclusion that the striking physical differences between the properties of amorphous and of crystalline matter must be referred to the existence in the latter of a most perfect and unique homogeneity of structure. The abstract geometrical study of homogeneous assemblages has accordingly been indispensable to the progress of the theory of crystal structure; its commencement may be dated from the pioneering work of Haüy, whilst the discovery of the 230 generalised point systems by Fedorov and Schönflies may be looked upon as its fitting culmination. However satisfactory this result may be, there was until quite recently no experimental method of elucidating the precise nature of the structural particles; of discovering whether they are atoms, molecules or molecular complexes; and still less of unravelling the exact structure of any particular substance in all its stereochemical details.

The recent discovery of Laue that the passage of a beam of *X*-rays through a crystal is signalised by the appearance of several secondary beams, opens up an entirely new field of experimental research, and clearly marks the beginning of an epoch in the history of crystallophysical science. The method has not only already led to most important results in the hands of its discoverer and his collaborators, but has also attracted the attention of other physicists who were working on the phenomena produced by the reflection of *X*-rays from a crystal face. The work which has been done in these two allied fields has already reached a suitable report stage. It has, moreover, deep chemical significance, since it promises to extend the domain of stereochemistry into the solid state of aggregation. In view of this, the writer feels that no special apology is needed for a fairly circumstantial account.

The development by Fedorov of a scientific method of classifying morphological data marks the chief progress to be noted in the province of chemical crystallography. Its need must have been felt by all those who are interested in the correlation of crystalline form with the chemical composition, for it is becoming increasingly

recognised that an almost unlimited choice of parametral ratios deprives any crystallographic description of that finality which is to be expected in a truly exact science. On the practical side the new classification has made it possible to identify any substance which has previously been measured—a distinction which is denied to all other physical properties; whilst on the theoretical side crystallographic (morphotropic) comparisons between substances are for the first time placed on a secure basis.

Coming to mineralogy proper, the discovery of several new minerals will have to be noted, as well as the synthesis of several others. Space does not permit of a systematic account of the various mineral analyses. Fortunately to a great extent they are to be found in the Abstracts for the year. Several very important pieces of work, as, for example, the experimental study of the polymorphous relationships of minerals, have had to be left over until next year.

The writer would take this opportunity of expressing his indebtedness to the previous reporter, Dr. A. Hutchinson, for much valuable advice as to the sources in which interesting information was likely to be found.

X-Ray Methods of Exploring Crystal Structures.

The Work of Laue and others on the Diffraction of X-Rays.

The experiments of Walter and Pohl[1] on the diffraction effects produced by the passage of *X*-rays through fine slits, led them to the conclusion that the wave-length of *X*-rays is of the order 10^{-9} cm., a value which is but little less than the estimated distance between contiguous molecules in a crystal. In view of this it occurred to Laue that the space lattice structure of a crystal might act as a grating towards *X*-rays, and thus lead to diffraction effects similar to those obtainable with an artificially ruled grating and ordinary light. This expectation was fully realised,[2] for it was found by a photographic method that if a small pencil of *X*-rays is allowed to impinge normally on a thin slice of a crystal, the pencil in its passage through the crystal is partly broken up into a number of secondary beams: the photographic plate which is placed behind the crystal shows a group of elliptical spots of varying intensity in addition to a round central spot due to the undeviated, primary beam. The arrangement of the spots is quite definite; moreover, by shifting the plate backwards or forwards

[1] B. Walter and R. Pohl, *Ann. Physik*, 1908, [iv], **25**, 715.

[2] W. Friedrich, P. Knipping and M. Laue, *Sitzungsber. K. Akad. Wiss. München*, 1912, 303; *Ann. Physik*, 1913, [iv], **41**, 971.

with respect to the crystal slice, the spot assemblage is proportionately enlarged or diminished, which proves that each spot is due to a rectilinearly propagated beam. On the other hand, any slight rotation of the crystal slice leads to a corresponding alteration of the pattern. Different substances give different patterns; the latter also depend on the direction of the slices from one and the same crystal.

Symmetry of the X-Radiogram.—The influence of the type of crystal structure on the diffraction effects produced is very clearly brought out by comparisons of radiograms obtained with different substances. The symmetry of the radiogram unmasks the general symmetry of the crystal in an unmistakable manner. Thus, in the photographs obtained with sections of the cubic zinc blende, there is a three-fold arrangement of spots when the slice is cut parallel to an octahedral face, whilst a four-fold arrangement is exhibited when the slice investigated has been taken parallel to a cube face. Similar patterns are obtained with other cubic substances, as, for example, rock salt, diamond, fluorspar, and cuprite.[3] On the other hand, the pattern with a crystal of the triclinic copper vitriol shows no symmetry whatsoever. Intermediate between these two extremes, we have the tetragonal nickel sulphate and tin stone exhibiting a four-fold pattern, and beryl (emerald), which, in accordance with its hexagonal symmetry, exhibits a six-fold arrangement—provided, of course, the primary beam of *X*-rays is directed along the principal axis of the crystal.

Effects produced in Hemihedral and Enantiomorphous Crystals.—Although zinc blende undoubtedly possesses the symmetry of a regular tetrahedron, the crystals behave as though they possess the full symmetry (holohedral) of the cube. It might therefore appear that the *X*-ray method is not sufficiently searching as to admit of the complete elucidation of crystal symmetry in all its details. Fortunately this is not always true. For example, the patterns afforded by slices of iron pyrites, FeS_2, and hauerite, MnS_2, cut parallel to a cube face, are in full accord with the presence of a two-fold (and not four-fold) axis of symmetry. Moreover, although the two minerals have the same symmetry, the patterns are not identical in every respect, thus proving that the specific natures of the atoms iron and manganese must be taken into account.

Experiments made with quartz crystals lead to results of greater chemical interest. If the primary beam is directed along the principal axis, the pattern of the radiogram is of a six-fold character, in so far as the position of the spots is concerned, but if the

[3] M. Laue and F. Tank, *Ann. Physik*, 1913, [iv], **41**, 1003.

relative intensity of the spots is taken into account, the arrangement is clearly made up of two sets of spots of different intensity—each of a three-fold nature. In other words, the rhombohedral as opposed to the hexagonal system is fully demonstrated; but there is no difference between a right- and left-handed crystal. If, however, the primary beam of *X*-rays is sent along the direction of a horizontal two-fold axis of symmetry, the differences between the right- and left-handed structures is betrayed, the pattern of the one being the mirror image of that of the other. A full description of these results has not been published; its appearance is eagerly looked for.

Interference Theory of Laue.—Laue supposes that the *X*-rays are of an electromagnetic character (non-corpuscular), and in their passage through the crystal set up vibrations, so that each crystal particle becomes a centre of wave disturbance. The resulting waves undergo interference, and a spot is produced in the radiogram when a set of vibrations are so close in phase as mutually to reinforce each other. The general equations governing the interference effect of a three-dimensional grating were developed, and their applicability was first tested in the case of a cubic slice of zinc blende, and somewhat later a similar mathematical analysis was carried out for a slice cut parallel to an octahedral face. Setting out from the assumption that the structure of zinc blende is modelled on the simple cubic lattice—an arrangement in which molecules are equally spaced along three sets of mutually perpendicular lines—the conclusion was drawn that the various spots are due to *X*-rays of five select wave-lengths, namely, $\lambda = 0{\cdot}0377a$, $0{\cdot}0563a$, $0{\cdot}0663a$, $0{\cdot}1951a$, and $0{\cdot}143a$, in which a represents the least distance between two molecules, and is equal to $3{\cdot}38 \times 10^{-8}$ cm. Each spot can then be accounted for as due to a summation, interference effect of innumerable molecules all disposed in a particular set of parallel planes in the crystal structure.

Laue's original deduction that the spectrum of *X*-rays is discontinuous, consisting, as it was supposed, of five definite wave-lengths, has not been confirmed by subsequent work. The general consensus of opinion now holds to the view that, although there is always present a certain amount of rays which are characteristic for each metal used as anti-cathode, yet the main and constant portion of the radiation is continuous within a large range of wave-lengths. It has been proved by Friedrich[4] that the radiograms are the result of the continuous spectrum, and not of the special radiation. The secondary beams, on the other hand, appear to be practically monochromatic, for Wagner[5] has recently found

[4] W. Friedrich, *Physikal. Zeitsch.*, 1913, **14**, 1079. [5] E. Wagner, *ibid.*, 1232.

that the radiogram produced by the further passage of these beams through a second crystal exhibits a relatively small number of spots. Now a difficulty arises in the application of Laue's theory to a continuous spectrum: the diffracted rays should not lead to the development of well-defined spots, but rather should cause a general darkening of the whole of the photographic plate. This difficulty has been removed by Debye,[6] who has pointed out that the crystal particles are not in reality stationary at the ordinary temperature, but must possess some vibratory or oscillatory movement by virtue of their heat energy. His mathematical analysis indicates that the intensity of the diffracted wavelets from most planes of the structure must be reduced to exceedingly low values owing to the molecular vibrations, and only in those planes in the structure which are characterised by a fairly dense packing of particles will the effect survive this weakening of intensity. Such planes are those which are characterised by low indices in a correct crystallographic description, and every spot in the radiogram corresponds with the diffractive action of a particular structural plane.

Other Attempts at Explanation.—Other attempts have not been wanting to account for the formation of the spots. The first of these explanations[7] is based on the corpuscular theory of *X*-rays. It is supposed that the corpuscles travel most easily in certain avenues of the crystal, each set of parallel avenues giving rise to a spot. It has been pointed out, however, in a paper[8] in which the principles involved in the analysis of a radiogram are very clearly described, that there are many fairly wide avenues in the crystal which are quite unrepresented by a corresponding spot in the radiogram. The second view advanced[9] is that the spots are due to reflections at the surface of cleavage cracks, which may be so fine as to escape detection by ordinary optical methods. Quite apart from the obvious drawback that one must presuppose the existence of cleavages which have never been observed in practice, there are other weighty considerations which militate against this view.[10]

A novel way of interpreting the action of the crystal on the *X*-rays as a pure reflection effect at internal planes of particles was early suggested by W. L. Bragg.[11] Although recent mathematical developments[12] prove that the Laue and Bragg views amount to much the same thing, yet the reflection view has provided

[6] P. Debye, *Ber. Deut. physikal. Ges.*, 1913, **15**, 857.
[7] J. Stark, *Physikal. Zeitsch.*, 1912, **13**, 973. [8] G. Wulff, *ibid.*, 1913, **14**, 217.
[9] L. Mandelstam and H. Rohman, *ibid.*, 220. [10] M. Laue, *ibid.*, 1075.
[11] W. L. Bragg, *Proc. Camb. Phil. Soc.*, 1913, **17**, 43.
[12] P. P. Ewald, *Physikal. Zeitsch.*, 1913, **14**, 465.

an extraordinary stimulus to investigation, since it has served to correlate the phenomena observed by the undoubted reflection of X-rays with the diffractive effects already described.

Interpretation of W. L. Bragg.—Each spot in the radiogram is described as due to a reflection of part of the energy of the incident beam of rays, by a set of parallel planes of atoms in the crystal. The planes that are most likely to act as reflectors are those which are densely packed with atoms, and the likelihood of obtaining an intense reflected beam is all the greater when the same conditions are fulfilled, as in the reflection of ordinary light from piles of parallel plates, namely, when $n\lambda = 2d \sin \theta$, where θ is the glancing angle (that is, 90°-normal angle) of incidence, d is the distance between successive parallel planes, λ is the wave-length of the radiation, and $n = 1, 2, 3, 4$, etc. When this equation is satisfied, the trains of waves reflected from each of the reflecting parallel planes are in the same phase and will reinforce each other, so that a reflected beam may be produced of sufficient intensity as to make a visible impression on the photographic plate. The position of a spot on the plate is in all cases determined by the direction of the internal plane serving as a reflector, the angle of incidence on that plane being equal to the angle of reflection. In the light of this interpretation, the Laue radiogram for zinc blende was reconstructed by Bragg, but it was concluded that the space lattice is not of the simplest cubic pattern. This conclusion has been confirmed by others, and has also been developed stereochemically by the author in a very interesting manner.

In studying the intensity of the spots, ingenious use has been made of the two-circle goniometer,[13] a cleavage piece of rock salt being mounted in such a position that the incident beam of rays impinges on internal cube and dodecahedral planes at the same angle. The spot derived from the cube plane is much more intense than that resulting from the dodecahedral plane. These two secondary rays were then allowed to impinge on a second crystal suitably mounted, and it was found that only one visible tertiary spot is produced, namely, that originating from a reflection of the secondary cube plane of the first crystal at the internal dodecahedral plane of the second crystal. This result could be predicted from Bragg's equation, and thus confirms its validity in an unmistakable manner.

A novel adaptation of the Laue experimental arrangement[14] is to replace the photographic plate by a barium platinocyanide screen, whereby the direction of the secondary beams are immediately shown by their fluorescent action on the screen. The elliptical

[13] G. Wulff and N. Uspenski, *Physikal. Zeitsch.*, 1913, **14**, 785.
[14] T. Terada, *Proc. Tokyo Math. Phys. Soc.*, 1913, **7**, 60.

arrangement of groups of spots corresponding with sets of internal reflecting planes having a common zone axis is especially striking, and the effect produced on the symmetry and general arrangement of the spots by a rotation of the crystal plate can be very conveniently studied.

The Work of W. H. and W. L. Bragg[14a] *and others on the Reflection of X-Rays by Crystals.*

The capital discovery that *X*-rays are strongly reflected at the surface of a crystal was made by W. L. Bragg.[15] A narrow pencil of rays was allowed to impinge on a cleavage surface of mica at a glancing angle of 10°, or, in other words, a normal angle of 80°, and after an exposure of only a few minutes, a photographic plate revealed a strongly marked spot due to reflection as well as the usual primary spot due to a direct passage through the crystal. The relative disposition of the primary and secondary spots showed that the angle of reflection is equal to the angle of incidence. A more sensitive method of estimating the intensity of the reflected ray was quickly devised by W. H. Bragg,[16] who replaced the photographic plate by an ionisation chamber, by means of which the strength of the reflected beam can be accurately gauged. The arrangement finally adopted is much the same as that of a spectrometer, the ionisation chamber replacing the ordinary telescope, so that the variation of the effect with the angle of incidence can be effectively studied. Confirmatory notices soon followed from other workers.[17]

The main results attained with the above apparatus[18] may be epitomised as follows: The law of equality of angle of incidence and reflection having been established, a series of experiments was instituted in which the ionisation chamber and incident beam were concomitantly varied with respect to the crystal plate, and the remarkable discovery was made that the intensity of the reflected beam varies enormously with the angle of incidence. Curves in which the intensity is plotted against the glancing angle of incidence, for crystals of iron pyrites, rock salt, zinc blende, potassium ferrocyanide, potassium dichromate, quartz, calcite, and sodium ammonium tartrate, all exhibit three peaks, A_1, B_1, C_1, very close to each other, which with larger angles may be succeeded by a

[14a] Prof. W. H. Bragg, of Leeds University, and his son Mr. W. L. Bragg of the Cavendish Laboratory, Cambridge.

[15] W. L. Bragg, *Nature*, 1912, **90**, 410. [16] W. H. Bragg, *ibid.*, 572.

[17] C. G. Barkla and G. H. Martyn, *ibid.*, 435, 647; H. G. J. Moseley and C. G. Darwin, *ibid.*, 594.

[18] W. H. and W. L. Bragg, *Proc. Roy. Soc.*, 1913, A, **88**, 428.

second, although less pronounced, system of peaks, A_2, B_2, C_2, and these by a third system, A_3, B_3, C_3. The conclusion is drawn that in addition to the general reflection of less intensity occurring at all angles of incidence, there is a selective reflection occurring at certain and very definite angles. This must be attributed to the existence in the primary *X*-rays of three monochromatic beams having specific wave-lengths. Each of these beams would be expected to suffer intense reflection when the equation $n\lambda = 2d \sin \theta$ is satisfied. As a matter of fact, the three peaks B_1, B_2 B_3 satisfy the equation most rigorously when $n = 1$, 2, and 3 respectively.

In the above experiments the anti-cathode was made of platinum. Other metals have since then been tried.[19] Since the incident angle of maximum intensity varies for each metal, it must be concluded that the wave-length of the special radiation is characteristic for each metal. Nickel, tungsten and iridium are found to give weaker characteristic beams. The most satisfactory material for anti-cathode proves to be rhodium,[20] which gives an intense radiation of two wave-lengths, one being far stronger than the other.

The effect of a change of the factor d (the distance between successive parallel, structural planes which cause the reflection) on the value of the intense, reflecting angle has been studied by examining plates cut parallel to the cube, dodecahedron and octahedron faces of rock salt. The values of the angles at which the B peak is observed have been measured, and by means of the reflection formula quoted above, the values $d_1 : d_2 : d_3$ can be calculated; they are found to be 1 : 0·718 : 1·16. Now it is a simple matter to calculate these ratios by pure geometry on the assumption of any given space lattice. Such theoretical values for the centred face lattice of the cubic system are 1 : 0·707 : 1·15. The reflection evidence then appears to be overwhelmingly in favour of this lattice in rock salt.

The above work also proves that the reflecting plane is not merely the geometrical surface of the crystal, but rather a succession (perhaps millions) of internal structural planes which lie under and parallel to the cleavage surface. This deduction is confirmed by some experiments[21] which have been instituted with quartz and gypsum, in which the surface was roughened to such an extent as to scatter ordinary light completely. On the contrary, the intensity of the reflected beam of *X*-rays is not weakened appreciably.

A further valuable contribution to our knowledge of selective

[19] W. H. Bragg, *Proc. Roy. Soc.*, 1913, **89**, 246.
[20] W. H. and W. L. Bragg, *ibid.*, 277.
[21] E. Hupka, *Ber Deut. physikal. Ges.*, 1913, **15**, 369.

reflection has been made by Moseley and Darwin[22] with an apparatus allowing of even more delicate measurements than that of Bragg. The latter's results have not only been confirmed, but by the use of finer slits it has been possible to resolve Bragg's second and third peaks, so that there are no less than five homogeneous series of *X*-rays (platinum anticathode), each yielding a reflection of the first, second, and third orders.

It was early observed that the spots in the Laue radiograms are striated, and on closer study[23] it has been found that striations are also exhibited by the spots given by the reflection method. The active cause of the striation appears to be a lack of homogeneity of the crystal, parts of the latter not being quite parallel to other parts.

With regard to the penetrative powers of the *X*-rays, it has been proved by Moseley and Darwin,[22] as also by Barkla and Martyn,[24] that there is little difference between the incident and reflected radiation. It must be noted, however, that a considerable amount of comparative work on the diffraction and reflection methods leads to the suspicion that the effects of the crystal are not entirely identical; although the diffracted rays retain their fluorescent action on barium platinocyanide, rays reflected from a cleavage flake of rock salt are inactive in this respect. Moreover, the wave-lengths as deduced by Laue are much lower than those obtained by the employment of the reflection method. It has therefore been suggested that the crystal may transform the incident *X*-ray energy into another order of wave-length.

Stereochemical Deductions from the X-Ray Methods of Investigation.

The probable arrangement of the molecules and atoms has been deduced by W. L. Bragg[25] for the binary compounds, zinc blende, rock salt, potassium chloride and bromide, and as far as the calcium atoms are concerned, in fluorspar and calcite also. Both the diffraction and reflection methods of investigation were employed. An analysis of the radiograms for all the substances enumerated with the exception of potassium chloride points to the centred face form of lattice. Now a considerable amount of evidence is also deduced in favour of regarding the heavy atoms as the diffracting centres; these atoms must then be arranged on

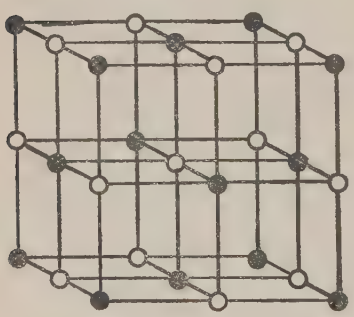
[22] H. G. J. Moseley and C. G. Darwin, *Phil. Mag.*, 1913, [vi], **26**, 210.

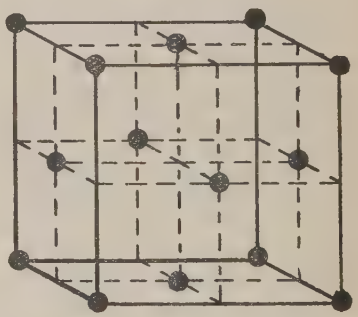
[23] G. Wulff and N. Uspenski, *Physikal. Zeitsch.*, 1913, **14**, 783; M. de Broglie, *Compt. rend.*, 1913, **156**, 1153; M. de Broglie and F. A. Lindemann, *ibid.*, 1461.

[24] C. G. Barkla and G. H. Martyn, *Proc. London Phys. Soc.*, 1913, **25**, 206.

[25] W. L. Bragg, *Proc. Roy. Soc.*, 1913, *A*, **89**, 248.

the centred cube pattern. In the binary compounds the lighter atoms can be arranged in the same pattern, and so disposed with the heavier atoms, that the assemblage as a whole becomes of the simplest cube pattern (see figure for sodium chloride, in which the black-point circles represent alkali metals, light-point circles the halogen atoms). It is then suggested that in potassium chloride, since the constituent atoms have weights of the same order of magnitude (39 and 35·5) both kinds of atoms act as diffracting centres, so that the radiograms should point to the simplest cubic arrangement. Strong confirmation is obtained from reflection experiments. In the case of fluorspar and calcite, the calcium atoms would appear to have the centred face arrangement; the position of the lighter atoms has not yet been determined. (Note: Calcite, being rhombohedral, can be regarded theoretically as a deformed cubic crystal.)





The structure of the diamond[20] has also been very thoroughly investigated, the results presenting many features of exceptional interest. The structure suggested is modelled on the centred face pattern, but with the following complications: half the total number of cells, selected in a symmetrical manner, have in addition a further point placed at their centres. The effect of this is that the successive planes of particles parallel to the octahedral faces are no longer equally distant from each other; in other words, the structure is no longer a space lattice, but an example of the Fedorov-Schönflies point systems. Since the diamond is of elementary composition, there can be no question as to the more powerful diffractive power of certain atoms as compared with others (as in the case of the halogen salts, zinc blende, etc.), and the evidence given in support of the structure advocated is very convincing. The chief chemical interest of the arrangement lies in the fact that each carbon atom throughout the whole structure is

immediately surrounded by four others in a regular tetrahedral manner.

The elucidation of the space lattice structure of a cubic crystal is a comparatively easy matter as compared with the difficulties to be expected in a crystal, say, of the monoclinic system, since not only has the type of lattice to be discovered, but also its relative dimensions, for the latter are not fixed by the symmetry. A praiseworthy attempt to determine the space lattice of gypsum, $CaSO_4,2H_2O$, has been made by Herweg,[26] who allowed a beam of *X*-rays to impinge on a cleavage plate at a glancing angle of 10°, and took photographs of the secondary beams due to reflection and refraction. From an analysis of the results it is inferred that the structure is founded on the monoclinic pinacoidal lattice, the three planes of the cell being parallel to {010}, {100}, and {$\bar{1}$01} of the usual setting.

It is hardly necessary to point out that, at any rate, some of the views which have been described cannot be regarded as final, but may possibly undergo considerable modification when further evidence has been accumulated. However this may be, there would seem to be little doubt that in the near future the employment and further development of *X*-ray methods will lead to a full knowledge of the disposition of the constituent parts of a crystal in most of its essentials.

Chemical Crystallography.

Crystallography can perhaps only boast of two occasions on which it has profoundly contributed to chemical theory, namely, when Mitscherlich discovered isomorphism, and Pasteur proved the correlation of optical activity in the amorphous condition and enantiomorphism of crystalline form. Later investigations, in so far as they relate to systematic researches, have served to multiply illustrations of these regularities. The great majority of published data, however, relates to isolated compounds, which have been more or less fortuitously placed at the disposal of the crystallographer by the synthetic chemist. The classification of this material according to chemical composition is obviously not likely to lead to any chemical progress. A classification according to the geometrical constants of the crystal may, on the other hand, result in the discovery of close crystallographic resemblances, and hence of similarity of chemical constitution, between substances, which might not otherwise be sought for, owing to the retarding influence of a periodical stereotyping of the general outlook—a feature, inseparable from the history of science, which is just as

[26] J. Herweg, *Physikal. Zeitsch.*, 1913, **14**, 417.

helpful in the early stages of discovery as it is detrimental to any important subsequent advance.

Difficulties in the Way of a Morphological Classification of Crystallographic Data.

It is self-evident that no classification can be regarded as satisfactory unless it is grounded on well-founded principles of an unambiguous character. The difficulties to be overcome in crystallography are of a special kind. The complex facial developments of most crystalline substances leads to an embarrassing number of angular values, from which a small selection has to be made for purpose of reference. In describing a crystal it is the usual practice to select certain of the angular values in order to calculate the parametral ratios $a:b:c$; which selection has hitherto been quite arbitrary, for other alternative angles might equally well be chosen yielding a different set of parametral ratios. Now the parametral ratios of two substances may on comparison exhibit a close numerical similarity; on the other hand, if such is not the case, it is as a rule quite an easy matter to produce from them, by a process of trial, other sets of ratios exhibiting a close correspondence. These facts show that any close correspondence of parametral ratios does not necessarily imply any real structural similarity in the two substances compared. The same remark applies equally well to the "topic axes" of Becke and the "equivalence parameters" of Barlow and Pope, which are in substance parametral ratios multiplied by a constant factor, having its origin in the molecular volume and valency volume respectively. Now wherever the primary object of a crystallographic investigation is to complete and add dignity to a chemical description of the substance, it matters little in what form the parametral ratios are given. If, however, the investigation is to do more than provide additional physical data and to attempt to elucidate the stereochemical interrelationships of two substances, it is of paramount importance that the "real" parametral ratios are employed—by "real" is meant those ratios which measure the relative edge lengths of the ultimate structural unit. It is true that in very close cases of chemical similarity, as, for example, those grouped under the term "isomorphism," the validity of a comparison can be established by means of certain crystallophysical methods, but in the most general case it is impossible to estimate the objective value of any alleged similarity.

One of the main channels of Fedorov's thirty years of activity has been directed towards the development of the principles of a scientific morphological classification. The crowning success of this

work, namely, the foundation of "crystallochemical analysis," has been appreciated in its general outlines in last year's report. Following is a short account of the principles adopted by Fedorov in his classification.

The Principles of Fedorov's Classification.

It is universally recognised that every crystalline substance is built up on a definite space lattice framework, although individual crystals may vary considerably as to the number and relative size of the faces. One of the fundamental properties of a space lattice structure is this: the relative massing of particles "reticular-density" varies enormously in different planes of the lattice. This property is made use of by Fedorov, who follows Bravais in the assumption that the faces actually developed correspond in the main with lattice planes having a high reticular density. This assumption is so sound theoretically that it is probably subscribed to in principle by all crystallographers. Its validity has been emphasised by the recent work of Friedel[27] on the form development of certain minerals, as also by the classical experimental work of Wulff[28] on the velocity of growth of a crystal in different directions. It is also in harmony with the accepted interpretation of the *X*-ray work on crystals. Now reticular density is not the only factor which influences the development of crystal faces; it is, however, the most important factor, and, what is very important, it is susceptible to exact mathematical formulation. Thus, if any particular space lattice be provisionally accepted for a given crystal, it is possible to verify by simple calculation how far the faces actually developed do correspond with planes of high reticular density; and since the values of reticular density are characteristic for each lattice, a choice can be quickly effected of the particular lattice which gives the highest all-round values for the faces developed. In actual practice probably two or three space lattices suggest themselves to the expert, and their relative merits are quickly estimated either by a simple graphical method,[29] or even by a consultation of tabular values which have been recently compiled.[30] The ratios of the three principal linear dimensions of this space lattice are nothing more or less than the true parametral ratios of the substance. They are deduced quite independently for each substance the composition of which may remain unknown;

[27] G. Friedel, *Bull. Soc. franç. Min.*, 1907, **30**, 326.
[28] G. Wulff, *Zeitsch. Kryst. Min.*, 1901, **34**, 449.
[29] E. S. Fedorov, *ibid.*, 1909, **46**, 245.
[30] W. J. Sokolov and D. N. Artemiev, *ibid.*, 1911, **48**, 377.

consequently there is no subjective attempt to induce a numerical similarity to confirm any previously conceived theory.

The trustworthiness of the above procedure is proved by the fact that the same set of parametral ratios is independently obtained for two crystals of one and the same substance, no matter whether the facial development is identical or not. Its fullest vindication, however, is afforded by cases of isomorphism; here the similarity of crystal structure demands a corresponding similarity of parametral ratios, and this always accrues in actual practice; in other words, the employment of Fedorov's principles unerringly discovers similarity where such indeed exists. It must be remembered that nothing need be known concerning the composition of the substance whilst the crystal analysis is being effected.

The second and concluding problem relating to the correct setting or description of each crystalline substance is that dealing with the appropriate orientation ("Aufstellung")[31] of the lattice with a view to uniformity of description; this question is evidently associated with the allocation of suitable indices to the faces, the choice of specific edges to serve as vertical, left to right, and front to back directions. Such questions are mainly of a purely methodological character; they are none the less of the greatest importance for the final classification.

It is in this connexion that Fedorov finds indispensable his theory of parallelohedra, enunciated in 1885.[32] The theory is really an extension of the space lattice, in that it attempts to endow the points of the space lattice with a corporeal shape expressing either the matter of the molecule or its domain of influence, so that the crystal structure ceases to be merely a collection of points, but becomes a system of figures, all alike and arranged in a parallel manner, filling space without interstices. Although the assignment of a particular shape to the crystal particle introduces debateable questions, and might superficially be deemed an unnecessary complication, yet the conception of the parallelohedron is of great help in co-ordinating into one organic whole crystals belonging to different systems of symmetry, and it is therefore a most valuable constructive implement. By means of it Fedorov is enabled to group together the whole of the crystal material into three grand types, an immense advance for the purpose in hand on the usually accepted seven systems. The nature of this grouping can be indicated without further reference to the parallelohedron.

In describing a tetragonal, rhombohedral (trigonal) or hexagonal

[31] E. S. Fedorov, *Zeitsch. Kryst. Min.*, 1904, **38**, 321.

[32] E. S. Fedorov, "Elements of the Theory of Figures" (Russ.), 1885; *ibid.*, 1911, **48**, 400.

crystal, it is customary to set up the crystal with the superior axis of symmetry in the vertical position, and also to apply a distinct system of indices to each of the three cases. On the other hand, the rhombic, monoclinic, and triclinic systems do not possess a superior axis of symmetry, and on this account, apart from the use of the tetragonal system of indices, there has hitherto been but little method in the descriptive setting of the crystals. The guiding principle now adopted by Fedorov is to set up the crystal in such a way as to bring out its approximation to one of the three higher systems, and then make a consistent use of the appropriate system of indices. To take the case of a monoclinic crystal, for example, when its space lattice has been determined by an analysis according to reticular density, the crystal is examined with respect to the angular values of the principal zones, and is then set up with that zone vertical which approximates most closely either to 90° or to 60°. The vertical axis then approximates to a four-fold or six-fold axis of symmetry; in the latter case the form development is scrutinised in order to discover whether it is best regarded as a three-fold or six-fold axis. It will now have been decided to which one of the three main groups of crystals the substance belongs –the tetragonaloid, trigonaloid, or hexagonaloid. The vertical direction having been settled, the left to right and front to back directions follow from definite rules; finally appropriate indices are allotted, and the description becomes complete and uniform.

The correct setting has been determined for all the substances hitherto measured (somewhat over 10,000), and the index entitled "Das Kristallreich," which is in active preparation, will be published in about eighteen months by the St. Petersburg Academy of Science. Crystallochemical analysis will then be within the reach of every crystallographer. In the index the matter is classified according to the tetragonaloid, trigonaloid, and hexagonaloid groups. The immediate basis of arrangement in each of these groups is the magnitude of the angle between the basal plane and the primary pyramid, which varies in crystals between the limits 10—80°; the division into subsections is made every half degree. The value of the angle mentioned determines any tetragonal, rhombohedral, or hexagonal crystal absolutely; with crystals belonging to a system with lower symmetry, the angular deviations from these ideal types are added. An ingenious system of symbols has been devised, each crystal being represented by a symbol which sums up its geometrical constants, and distinguishes it from any other crystal.

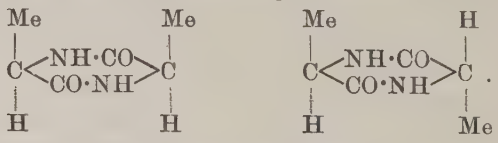
It is not suggested that Fedorov's method is absolutely infallible.

Isolated cases (actually less than 1 per cent.) present themselves, in which the correct setting cannot be determined with finality. One result of the classification should be to stimulate anew the correlation of crystalline form and chemical composition, since the material to be compared has now been classified on a sound basis. Another interesting result of the work[33] has been to prove the chemical identity of several "pairs of substances" which have been hitherto supposed by chemists to be different compounds.

Enantiomorphism.

Enantiomorphism of molecular configuration has been discussed in its general aspect by Barker and Marsh,[34] who have pointed out that the adoption of any single criterion fails to meet all cases which might arise. Thus absence of a plane of symmetry or of a centre of symmetry does not of necessity imply enantiomorphism. The complete conditions for enantiomorphism, and hence of appearance in optically active forms, are the simultaneous absence of a plane of symmetry, a centre of symmetry and an alternating axis of symmetry. The reasons for this are best appreciated by constructing models of objects which are in themselves completely asymmetric, as, for example, gloves; it is found that for any model possessing any one of the three specified elements of symmetry, an equal number of right and left handed gloves are required, every such assemblage being internally compensated.

It is also emphasised that an enantiomorphous assemblage need not be entirely asymmetric, for enantiomorphism is not incompatible with the presence of an ordinary, as opposed to alternating, axes of symmetry. An interesting case illustrating this point is that of the *cis*- and *trans*-forms of 1 : 4-diketo-2 : 5-dimethylpyrazine, the *cis*-form of which, although possessing a two-fold axis of symmetry,



is optically active. The *trans*-form (alanyl anhydride), on the other hand, has a centre of symmetry, and as a result is internally compensated. Exactly similar possibilities are to be met in lactide and succinosuccinic ester. Again, many of the co-ordinated compounds which have been recently so successfully resolved by Werner possess ordinary axes of symmetry; for example, the complex chromium oxalate group, $Cr(C_2O_4)_3$, in the optically active

[33] E. S. Fedorov, *Zeitsch. Kryst. Min.*, 1912, **50**, 573.
[34] T. V. Barker and J. E. Marsh, *T.*, 1913, **103**, 837.

potassium chromium oxalate, has a three-fold (trigonal) as well as three two-fold (digonal) axes of symmetry.

The same paper contains a discussion of the structural relationships which must accompany the appearance of optical activity in the crystalline condition, and it is concluded that the optical activity of crystals of sodium chlorate and bromate, Schlippe's salt, $Na_3SbS_4,9H_2O$, sodium uranyl acetate, $NaUO_2(C_2H_3O_2)_3$, sodium dihydrogen phosphate, NaH_2PO_4,H_2O, as well as in magnesium sulphate, $MgSO_4,7H_2O$, must be referred to enantiomorphism of the molecule. Suitable spacial formulæ are suggested which are modelled on an extension of Werner's theory of co-ordination.

Copaux's conclusion that *d*- and *l*-crystals of sodium chlorate have different solubilities has been called into question by Kreutz,[35] who argues that Copaux's results require a new interpretation. Copaux measured the relative increase in area of *d*- and *l*-crystals while growing under the same conditions, but this is not the same as measuring the thickness deposited on the faces since the crystals employed were not cubes but rectangular parallelepipeda. The new interpretation of the experimental results leads to the conclusion that an equal increase of thickness obtains with the two antipodes. Moreover, Kreutz found that saturated solutions in contact with either antipode have the same concentration.

An explanation has still to be found for the well-established and interesting observations of Wyroubov and of Copaux on the silicotungstates; with many of these substances *l*-crystals are very rarely met with.

A valuable contribution to the crystallography of optically active substances has been made by Hutchinson,[36] who has described the rhombic *d*-tetrahydroquinaldino-*d*-methylenecamphor and its antipode, as well as the monoclinic, partly racemic *d*-tetrahydroquinaldino-*dl*-methylenecamphor and its enantiomorph. Owing to the absence of hemihedral facets, the former pair of antipodes are geometrically indistinguishable, but in the latter pair, enantiomorphism is elegantly indicated by the polar character of the crystals. A close morphotropic relationship is found to exist between the four compounds.

Isomorphism.

A further contribution to the well-known series of the hexahydrated double sulphates and selenates has been published by Tutton,[37] who has investigated the geometrical and optical characters of Mohr's salt, $(NH_4)_2Fe(SO_4)_2,6H_2O$. The results obtained

[35] St. Kreutz, *Zeitsch. Kryst. Min.*, 1913, **51**, 236.

[36] A. Hutchinson. See W. J. Pope and J. Read, *T.*, 1913, **103**, 1515.

[37] A. E. H. Tutton, *Proc. Roy. Soc.*, 1913, A, **88**, 361; *A.*, ii, 603.

completely confirm the conclusions previously derived from a study of the ammonium salts of the same series, and again prove that, although not belonging to the eutropic series potassium, rubidium, and cæsium, the structural function of the ammonium radicle is very similar to that of the three alkali metals, so that the isomorphism is of a very close character. Generally speaking, the ammonium salt shows greatest approximation in its physical characters to the corresponding rubidium salt. This constant isomorphous replaceability of a single metallic atom by a radicle consisting of no less than five atoms is probably the most remarkable regularity known to the crystallographer.

An investigation which has considerable theoretical interest as bearing on the miscibility of isomorphous substances is that of Schobert,[38] who has studied the equilibria at high temperatures of binary mixtures of sodium chloride, bromide, and iodide, as well as the ternary systems obtained therefrom by the addition of water as the third component. Fusions of sodium chloride and bromide afford an uninterrupted series of mixtures with a eutectic lying at 731°—Roozeboom's type III. The miscibility again is perfect from solution above 60°, but at temperatures below 50·7°, which marks the appearance of the dihydrate of sodium bromide, the miscibility is of necessity restricted, since we have to deal with an isodimorphous pair. The transition temperature of NaCl into $NaCl,2H_2O$ is at 0·15°, below which there is a possibility of perfect miscibility, since the dihydrates are isomorphous. Experiments proved, however, that there is a gap in the series. Remembering that the percentage difference of halogen is much less in the hydrates than in the anhydrous form, it is seen what a large influence must be attributed to temperature in the degree of isomorphous miscibility.

Another investigation of a similar character, which was also carried out in the Leipzig Mineralogical Laboratory,[39] relates to mixtures of sodium and potassium chromate both in presence and absence of water. These substances behave in a manner precisely analogous to that of the corresponding sulphates, and form a double salt, $3K_2CrO_4,Na_2CrO_4$, chromeglaserite, which is able to take up isodimorphously a certain amount of sodium chromate. At very high temperatures the sodium and potassium salts form an uninterrupted series of mixed crystals, which on cooling break up into chromeglaserite and excess one of the simple chromates.

A valuable contribution to the crystallography of the rare earths has been made by Rodd,[40] who has described a number of iso-

[38] E. Schobert, *Diss.*, Leipzig, 1912.
[39] E. Flack, *ibid.*
[40] E. H. Rodd, *Proc. Roy. Soc.*, 1913, A, **89**, 292 ; *A.*, i, 1167.

morphous hydrated 2 : 5-dichloro- and dibromo-benzenesulphonates of lanthanum, neodymium, praseodymium, gadolinium, and didymium; also the trihydrate of 2 : 5-dichlorobenzenesulphonic acid as well as its potassium, sodium, zinc, and magnesium salts. Of these compounds the two last-mentioned are closely isomorphous, and the data given fully prove the isomorphous replaceability of chlorine and bromine.

The author attempts to bring the material into consonance with the Barlow-Pope theory, and has recourse to methods of interpreting the goniometrical results, which are open to criticism. For example, having initially discarded the most simple indices in order to get a fairly close value for the monoclinic angle β, the author subsequently employs the fractions $2a/3,c/4$ for the sodium salt, and $3a/2,c/2$ for the potassium salt of the dichloro-acid, and the desired morphotropic resemblances are established between the two salts and the parent substance benzene. The author is here following the example of Barlow and Pope in regarding this device as legitimate, but it has been lost sight of that the geometrical development of the two substances, as expressed by indices, now acquires the extravagant form: {100}, {320}, {342}, and {302} for the potassium compound, and {001}, {803}, {403}, {230}, {4.12.3} and {441} for the sodium salt; and the absence of any face common to the two crystals appears to make hazardous any comparison whatsoever.

Morphotropic Resemblances.

The term morphotropy was introduced by Groth in 1870 to connotate the study of the specific effect on crystalline form brought about by the substitution of hydrogen in benzene by the halogens or by groups like OH, NO_2, CH_3, etc. Although such substitutions lead to a somewhat fundamental alteration in the crystallographic constants, yet in a great many cases the effect appears to be concentrated on one of the parametral ratios, the other remaining relatively unchanged. Since then the meaning of the term has been somewhat widened, so that it has now practically come to mean the general study of the correlation of crystalline form and chemical composition. In this widened sense enantiomorphism and isomorphism are but particular cases of morphotropy, in which the resemblance is highly pronounced.

For the first time in its history the general subject of morphotropy has been placed on a scientific basis as a result of Fedorov's work on the correct description of crystals. During the year two

important papers[41] have been contributed, in which various topics of interest are discussed. It is pointed out that it is impossible to set a limit to isomorphism, the variations of angle for chemically, very closely related substances ranging from very small to very large values. Many cases are given in which two substances crystallise in different systems and yet exhibit a very close similarity; this is an argument against regarding a difference of system as a barrier against isomorphism. Another conclusion is that a difference in the water content of hydrated compounds is compatible with a close similarity of crystalline form. It appears to the writer, however, that many water determinations are faulty, and that more accurate determinations might bring the formulæ of many compounds into harmony.

As a direct result of his classification Fedorov is enabled to cite a large number of cases of similarity between substances which have not hitherto been regarded as similarly constituted, although a general, if only empirical, analogy is easily apparent, and the term "*isotectonic*" is suggested to meet such cases. The following selection of isotectonic compounds will perhaps bring home the nature of the chemical resemblance:

K_2ZnCl_4, K_2SO_4, $CsHgBr_4$, $(Me_4N)_2CuCl_4$.	$Hg(OH)ClO_3$, $KFBF_3$.
$CsNO_3$, $CaSiO_3$.	MgF_2, RuO_2, $Hg(CN)_2$.
Mg_2SiO_4, Al_2GlO_4.	$KCrO_3F$, $KRuO_4$.

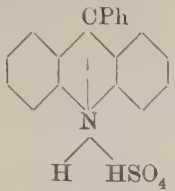
It seems likely that compounds like the above will repay further study, and perhaps be of use in recasting current views on valency.

Chromoisomerides.

The term "chromoisomerism" has been proposed and employed for some years by Hantzsch in connexion with substances crystallising in several modifications, which are mainly distinguishable from each other by colour. The subject has been already criticised in these reports,[42] where it was pointed out that the experimental evidence for isomerism, as opposed to polymorphism, is very slight. The isomerides do not appear to possess any separate stable existence in solution, and the variously coloured forms with any given solvent yield chemically and physically identical solutions. Slight differences in the absorption spectra in the ultra-violet region are, however, observable. The explanation given by Hantzsch for the various isomerides is founded on Werner's theory of valency isomerism.

[41] E. S. Fedorov, *Zeitsch. Kryst. Min.*, 1913, **52**, 11, 97.
[42] *Ann. Report*, 1911, 54.

One of the most striking cases of chromoisomerism, namely, that of phenylacridonium hydrogen sulphate:



which is generally quoted as exhibiting a yellow, red, and green modification, has been recently subjected to a very thorough crystallographic investigation by Pauli,[43] the results of which confirm the view adopted on the previous report. The crystallisation was studied from various mixtures of the three solvents, water, sulphuric acid, and alcohol, and no less than six varieties are obtained differing either in colour or in crystalline shape, namely, stout, red, monoclinic crystals, brown plates, yellowish-brown needles, green, triclinic crystals, green plates, and green needles. The variety which separates from solution is determined by the proportions of the three solvents; a large alcoholic content, for example, favours the formation of red crystals. Goniometrical measurement and determination of the crystallo-optical properties as well as the specific gravity proved the identity of the first three varieties on the one hand, and the three latter varieties on the other hand. The crystallographic constants for the red (brown and yellow) are $a:b:c=2{\cdot}398:1:2{\cdot}141$; $\beta=98°5'$; whilst for the three green varieties the constants are $a:b:c=0{\cdot}907:1:0{\cdot}739$; $\alpha=118°10'$, $\beta=114°32'$, $\gamma=59°42'$. The colour of each form appears to depend somewhat on the degree of fineness of the material, a fact which is well known in mineralogy. Again, the same crystals may appear differently tinted when viewed in different directions; this is due to the strong pleochroism of the crystals.

The red and green crystals, on keeping, become covered with a yellow coating; this was held by Hantzsch to be an isomeric change into the yellow modification. The yellow coating is now found to be crystallographically identical with phenylacridine, so that the change really denotes a hydrolysis of the acid sulphate.

The red crystals are stable on heating up to the melting point, 265°, but with the green crystals a remarkable colour change begins at 162° and is complete at 175°, when the colour has become reddish-yellow. On further heating, the tint becomes more and more red.

The results obtained by slowly cooling the fused substances are independent of the original modification employed. Two forms

[43] O. Pauli, *Diss.*, Leipzig, 1912.

appear, the first being brownish-yellow and optically identical with the monoclinic red modification. The second form is greenish-yellow and optically identical with the green, triclinic modification.

The above investigation has been described in some detail because it illustrates very well how far a crystallographic investigation may bear on a point of chemical theory; the acid sulphate of phenylacridine must be regarded as dimorphous and not trichromoisomeric.

Mineralogy.

Thermal Studies of Minerals.

The application of the phase rule to the investigation of the behaviour of mineral mixtures continues to attract much practical attention, especially on the part of American workers, and the present year is distinguished by at least one really first-class piece of work. The methods of investigation have been so much improved that the accuracy of a high temperature determination may now be confidently trusted. The great disagreement between these latest thermal data and those resulting from former researches prove that the latter cannot pretend to much accuracy, but must be looked upon as pioneering work of an orientative character. The importance of the subject, especially to the geologist, can scarcely be overrated, inasmuch as it touches on some of the most fundamental problems connected with the natural history of rocks. Many petrological regularities have already met with a satisfactory explanation on a physico-chemical basis, apropos of which it will be sufficient to quote from Bowen's paper: "In view of the very great quantitative importance of the plagioclases in igneous rocks it is a matter of some satisfaction to find them obeying the laws of physical chemistry to the extent here found."

Plagioclase Felspars.—The important work of Bowen[44] on the melting phenomena of these minerals deals with the determination of the solidus and liquidus curves for mixtures of albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$. In order to determine the temperature at which a given mixture begins to melt, it was steadily kept at a certain temperature for half-an-hour, and then suddenly cooled by quenching in mercury. Any melting is easily detected optically by the presence of glass in the specimen, due to the rapid quenching. By successively trying higher and higher temperatures until the presence of glass is noted, the point on the solidus curve is thereby obtained. Again, by raising the temperature still higher, until no trace of crystalline material remains after quenching, the whole having been melted and then solidified into glass, the corresponding point in the liquidus curve may be realised.

[44] N. L. Bowen, *Amer. J. Sci.*, 1913, [iv], **35**, 577; *A.*, ii, 613.

The temperatures were determined by a thermo-couple, and the results are accurate to about 5°. The melting points of albite and anorthite were found to be $1100 \pm 10°$ and $1550 \pm 2°$ respectively (for other data see the abstract). Independent confirmation of the composition of the liquid phase was obtained by a determination of the refractive index of the glass by Becke's immersion method. The values so obtained were compared with those of Larsen,[45] and the agreement is extraordinarily good. The author further tested his results in the light of the equations deduced thermodynamically by van Laar, which admit of a calculation of the solidus and liquidus points from the latent heats and absolute melting points of the pure components. The agreement is again very striking.

Of the author's two principal conclusions, the first is that albite and anorthite must have the same molecular complexity in the liquid, as also in the solid state, but the complexity in the two states may be quite different. The second conclusion relates to the frequently observed zonal development of the natural plagioclases—the nucleus of the crystals is practically always relatively rich in anorthite, the outer layers becoming richer and richer in albite. Now the paths of the two curves are such that the difference in composition of a crystal and the liquid in equilibrium with it may differ by as much as 40 per cent.; a magma consisting initially of 50 per cent. of each constituent will deposit crystals containing 81 per cent. of anorthite; and, since diffusion in the solid crystal is very slow, its composition will not respond to alterations of composition set up in the magma, the net result being that the crystal will become covered with successive layers of material relatively poor in anorthite.

The melting-point curve of the naturally occurring mixtures of orthoclase and albite has been determined by means of the Doelter heating microscope.[46] Most of the minerals contain small amounts of lime in the form of anorthite, which is found to have considerable effect in lowering the melting point. The melting interval was about 25°, and the lowest temperature registered was met with in the case of cryptoperthite from Laurvik with a 58 per cent. albite content, thus confirming Vogt's opinion that this represents the eutectic of the series. The author believes, however, that the series corresponds with type III of Roozeboom's classification, and not V, as suggested by Vogt.

Miscellaneous Fusions.—The thermal investigation of mineral mixtures is undoubtedly beset with great difficulties, some of which have been recently subjected to detailed investigation.[47] Mineral

[45] E. S. Larsen, *Amer. J. Sci.*, 1909, **28**, 283; *A.*, 1909, ii, 841.

[46] E. Dittler, *Tsch. Min. Mitt.*, 1912, **31**, 513.

[47] H. Leitmeier, *Zeitsch. anorg. Chem.*, 1913, **81**, 209; *A.*, ii, 613.

products are seldom pure, but contain in solid solution other materials of either much higher or lower melting point; it is thus to be expected that different values are frequently obtained by different observers. Again, the melting operation is generally a gradual process; sintering (passage into a solid, amorphous form) generally takes place, and a clear liquid is not obtained until a much higher temperature is reached. The sintering point may vary by as much as 80°, depending on the relative coarseness of the grain. The author prefers to take the lower sintering point as the melting point rather than the upper point of mobile liquefaction, basing his choice on the greater precision which can be attached to a change, crystal $\longrightarrow$ amorphous, than to a change, glassy-amorphous $\longrightarrow$ liquid-amorphous. The selection of the lower temperature receives further justification as a result of some new determinations, in which the mineral was heated to a point at which it just begins to sinter, and then kept at that temperature for twelve, twenty-four, or even forty-eight hours. It was thus possible to transform a crystal of St. Gothard adularia (orthoclase) into a viscous liquid at 1145°—the temperature at which it first showed signs of sintering.

The thermal and optical behaviour of the sulphates of calcium, strontium, barium, and lead—that is, the minerals anhydrite, celestine, barytes, and anglesite—as also of the binary mixtures of each of these sulphates, as well as glucinum sulphate, with potassium sulphate, has been studied in great detail by Grahmann.[48] It is found that all the four mineral sulphates are reversibly dimorphous with transition temperatures at 1193°, 1152°, 1149°, and 852° respectively. The high temperature modifications are monoclinic, and probably all isomorphous. With the exception of $K_2SO_4 + PbSO_4$, the binary systems are signalised by the appearance of a double sulphate 1 : 2, analogous to the mineral langbeinite, $K_2SO_4,2MgSO_4$, in composition, but not in crystalline form. The calcium, strontium, and lead langbeinites, however, are isomorphous; moreover, each yields another modification at high temperatures, the points of transition lying at 936°, 750°, and 544° respectively.

A large number of thermal investigations of binary mixtures has been carried out, chiefly in Bruni's laboratory, by Italian workers. Although highly interesting, they cannot be entered into here, since they have little, if any, direct mineralogical bearing. The investigation of Zambonini[49] on the miscibility of the tungstates of cerium and lead is of some mineralogical importance,

[48] W. Grahmann, *Diss.*, Leipzig, 1912.

[49] F. Zambonini, *Atti R. Accad. Lincei*, 1913, [v], **22**, i, 519; *A.*, ii, 596.

since it is often assumed that these metals can replace each other isomorphously in certain minerals. The two substances were, indeed, found to yield an uninterrupted series of mixed crystals—Roozeboom's type I.

Hydrothermal Formation of Minerals.

A review of the present position in this branch of work by Morey and Niggli[50] has appeared during the year. The paper contains a critical bibliography of all the syntheses hitherto effected, and must be invaluable to those who take an active interest in the subject. It must be remembered that the reactions often take place at temperatures far above the critical point of water, whilst the solid phases may have melting points at still higher temperatures. The important question as to the equilibrium rôle played by water receives an adequate discussion. The work of Smits[51] on the system anthraquinone–ether at temperatures below and above the critical temperature of ether has a very cogent bearing on this point, from which work it is inferred that too much importance has all along been attached to the significance of the critical point of water on questions of silicate equilibria. Owing to the very small solubility of silicates, the passage of the water into the critical condition can perhaps have but little effect on the relative stability of the minerals. It is possible that the main part of the chemical change takes place in the solid phase, and this, in turn, must especially favour the formation of products which are not absolutely stable, but merely metastable. The frequent formation of tridymite when quartz is to be expected is thus explained. Again, the stubborn persistence of metastable phases explains the differences noted in the products by taking the initial materials in a different chemical form, although in the same ultimate quantitative proportions. The authors' final conclusion is that the problems of hydrothermal silicate syntheses can physico-chemically be worked out on the same lines as van't Hoff's researches on the Stassfurt deposits.

With regard to the temperatures which are most favourable for the separation of various minerals, it appears that the zeolites are easily prepared at temperatures up to 200°. The region between the limits 300—550° is characterised by the frequent formation of quartz, the felspars albite and anorthite, and analcite; but the simultaneous formation of those minerals which frequently accompany the above in nature, namely, the pyroxenes, amphiboles,

[50] G. W. Morey and P. Niggli, *J. Amer. Chem. Sci.*, 1913, 35, 1086; *A.*, ii, 861.
[51] A. Smits, *Zeitsch. physikal. Chem.*, various papers.

micas, magnetite, hæmatite, corundum, etc., has been only very seldom noticed.

The study of the system $K_2O + Al_2O_3 + SiO_2 + H_2O$ by E. Baur has been noticed in a previous report.[52] The effect of the addition of ferric oxide has now been studied by Niggli,[53] and with the interesting result that the best crystallised product is potassium ægirine, $KFe(SiO_3)_2$. The heating was carried out in a steel bomb for one to two days to a temperature of 450°. The identifiable minerals accompanying K-ægirine were hæmatite, orthoclase, and hydrated K-nepheline. A relatively low percentage of alumina is indispensable for the appearance of K-ægirine, which, by the way, does not occur in nature, although its sodium analogue, $NaFe(SiO_3)_2$, is an important member of the pyroxene group. Its non-observance in nature is, perhaps, due to the fact that magmas containing a large amount of potash as opposed to soda are also always rich in magnesia and lime; the latter unite with the whole of the iron to form augite, leaving none for the potash, which then combines with the alumina to form leucite, $KAl(SiO_3)_2$.

Potassium nepheline, $KAlSiO_4$, apparently identical with the little-known mineral kaliophilite, has been synthesised by Friedel[54] by heating in a steel, copper-lined tube to a temperature of 600° a mixture of muscovite and a solution of potassium hydroxide. The crystals obtained are hexagonal, and very similar in their general properties to ordinary soda nepheline, $NaAlSiO_4$. The author has previously shown that if the reacting substances contain even a very small amount of soda, the only product is a practically pure soda nepheline. This is in harmony with the common occurrence of the latter in nature and the rare occurrence of kaliophilite. The author is of the opinion that the excess of silica found in all nephelines has not yet received a satisfactory interpretation.

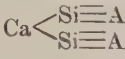
Anhydrothermal Syntheses of Minerals.

The most interesting synthesis of this class is certainly that of anorthite, $CaAl_2Si_2O_8$, effected by Reynolds[55] from a very novel source. The mainspring of this work is the author's previous extensive researches on silicon organic compounds, in which it has been shown that the group SiN (analogous to CN) is an integral part of many synthetic substances.

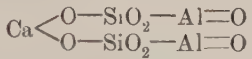
Attempts were first made to prepare the compound Si_2Al_2 analogous to cyanogen by the combination of the free elements, but

[52] *Ann. Report*, 1911, 247.
[53] P. Niggli, *Zeitsch. anorg. Chem.*, 1913, **84**, 31.
[54] G. Friedel, *Bull. Soc. franç. Min.*, 1912, **35**, 471 ; *A.*, ii, 422.
[55] J. E. Reynolds, *Proc. Roy. Soc.*, 1913, A, **88**, 37 ; *A.*, ii, 212.

with imperfectly satisfactory results. In presence of calcium, however, a well-defined substance is formed, $Ca(SiAl)_2$, termed calcium silicalcyanide, which from its general chemical behaviour must be regarded as entirely analogous to calcium cyanide, $Ca(CN)_2$, in constitution. When subjected to the action of a current of oxygen and steam at a high temperature, the compound took up eight atoms of oxygen to form $CaAl_2Si_2O_8$, which when fused and slowly allowed to cool gave a pure specimen of anorthite, identity being established by chemical and optical methods. The derivation and constitution of anorthite as given by the author are expressed in the following scheme:



Calcium silicalcyanide.



Anorthite.

Attempts were also made to isolate sodium silicalcyanide with a view to the ultimate synthesis of albite, but were fruitless, owing to some extent to the volatility of sodium at the high temperature required.

New Minerals.

Chillagite.[56]—The mineral was found in Christmas Gift North Mine, Chillagoe, in the form of tabular, translucent, yellow plates, together with cerussite. The crystalline form has not been thoroughly determined, but appears to be tetragonal. Analysis corresponds with the formula $PbWO_4,PbMoO_4$. Until further crystallographic details are given, it must remain uncertain whether the mineral is a new species, or merely an isomorphous mixture of stolzite and wulfenite.

Custerite.[57]—The occurrence is in a limestone-granite porphyry contact zone near Mackay, Custer Co., Idaho, the associated mineral being magnetite, with a certain amount of garnet and diopside. The mineral occurs in fine, granular masses, and appears to weather into calcium carbonate; there are three distinct cleavages parallel to the forms {110} and {001}, and their relative inclinations argue for the monoclinic system. This conclusion was confirmed by an optical determination carried out on the Fedorov universal stage. Obt. Bx. the symmetry axis; positive Ac. Bx. nearly normal to {001}, $2V_{Na} = 60°$, $2E = 105°$, $\beta = 1{\cdot}59$, $\gamma-\alpha = 0{\cdot}0121$, $H = 5$, $G = 2{\cdot}91$. Repeated twinning parallel to {001}.

Analysis points to the formula $[Ca(OH,F)]_2SiO_3$, the ratio OH : F being about 4 : 3. The mineral is therefore related to zeophyllite, cuspidine, and hillebrandite.

[56] A. T. Ullmann, *J. Roy. Soc., New South Wales*, 1912, **46**, 186; *A.*, ii, 867.

[57] J. B. Umpleby, W. T. Schaller and E. S. Larsen, *Amer. J. Sci.*, 1913, [iv], **36**, 385; *A.*, ii, 1063.

Delafossite.[58]—This mineral was first described from Siberia by Friedel in 1873, but has been hitherto looked upon as a doubtful species. It has now been found at Bisbee, Arizona, in platy crystals, constituting a combination of {111} large and {100} of the rhombohedral system: $a:c=1:1{\cdot}94$. It is found in a white kaolin and ferruginous clay at the fourteenth level of the Hoatson shaft of the Calumet and Arizona property, near Copper Queen Mine. The composition is that of a cuprous metaferrite, $Cu'Fe'''O_2$.

Epidesmine.[59]—This new zeolite occurs with orthoclase as a crystalline crust on calcite at the Gelbe Birke Mine, Schwarzenberg, in the Saxon Erzgebirge. Analysis points to exactly the same formula as stilbite, and the two minerals in all probability present a case of dimorphism. The symmetry is rhombic with a development of the three pinacoids. On some specimens a single inclined face, say, (111), was observed, from which the values $a:b:c=0{\cdot}7315:1:0{\cdot}4181$ are deduced provisionally.

Grothine.[60]—This new mineral, which has been named in honour of Prof. P. Groth, occurs in a metamorphic limestone at Nocera and Sarno in Campagnia, Italy. The colourless crystals belong to the rhombic system with $a:b:c=0{\cdot}4575:1:0{\cdot}8484$. The habit is tabular, parallel to $b\{010\}$. Forms: $b\{010\}$, $c-\{001\}$, $m-\{110\}$, $e-\{101\}$, $o-\{111\}$, and $r-\{121\}$. $D=3{\cdot}085$. Optics, positive Ac. Bx. perp. to (100), ax. pl. (001); 2E medium, $\rho<v$. The amount of material as yet available does not admit of a quantitative analysis. Qualitative tests points to an alumosilicate of calcium with a trace of iron.

Hodgkinsonite.[61]—This mineral is a hydrated zinc-manganese silicate, and occurs in the Parker Mine at Franklin Furnace, New Jersey. It is always associated with barytes in the granular willemite-franklinite ore of that locality. The crystals are monoclinic with $a:b:c=1{\cdot}539:1:1{\cdot}1165$; $\beta=84°33'$. The forms are: $m-\{110\}$, $s-\{011\}$, and $r-\{221\}$, together with corrosion planes having complicated indices. $D=3{\cdot}91$, $H=5$; mean refractive index $=1{\cdot}73$, ax. pl. (010). The colour ranges from a bright pink to a pale reddish-brown; the lustre is vitreous, the streak white. Analyses agree with the formula $3RO{\cdot}SiO_2,H_2O$, where R = Zn and Mn in the ratio 2:1; also present small amounts of lime and magnesia.

Maucherite.[62]—The locality is Eisleben, Thuringia, the mineral

[58] A. F. Rogers, *Amer. J. Sci.*, 1913, [iv], **35**, 290; *A.*, ii, 419.

[59] V. Rosický and S. Thugutt, *Centr. Min.*, 1913, 422; *A.*, ii, 783.

[60] F. Zambonini, *Atti R. Accad. Lincei*, 1913, [v], **22**, i, 801.

[61] C. Palache and W. T. Schaller, *J. Washington Acad. Sci.*, 1913, **3**, 474.

[62] F. Grünling, *Centr. Min.*, 1913, 225; *A.*, ii, 516; A. Rosati, *Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 243.

being found in the copper shales. The symmetry is tetragonal; $a:c=1:1{\cdot}1185$; forms: $c-\{001\}$, $t-\{223\}$, $p-\{445\}$, $o-\{111\}$, $d-\{554\}$, $v-\{443\}$, $e-\{553\}$, $l-\{221\}$, $g-\{552\}$, $h-\{331\}$, and $b-\{441\}$. Analysis agrees with the formula Ni_3As_2. A product having this composition is often met with in metallurgical processes, and has been variously termed "Nickelspeis" and "Placodin," and it is interesting to note that Rosati has been able to show that the lately discovered mineral and the long known artificial product are crystallographically identical.

Pyroxmangite.[63]—The locality is near Iva, Anderson Co., South Carolina, where the mineral occurs in brown cleavage masses with a cleavage angle equal to 88°10′. The system is probably triclinic. Although analysis agrees with the formula $(Mn,Fe)SiO_3$, the optical properties differ from those of rhodonite, and the authors accordingly believe the mineral to be a new species of the manganese pyroxenes.

T. V. Barker.

[63] W. E. Ford and W. M. Bradley, *Amer. J. Sci.*, 1913, **36**, 169; *A.*, ii, 869.

RADIOACTIVITY.

In the last section of the 1910 Report, "Chemical Relationships of the Radio-elements," the existence of groups of radio-elements possessing identical chemical properties was shown to foreshadow "some embracing generalisation which will throw light, not only on radioactive processes, but on the elements in general and the Periodic Law."[1] In 1911 the first step in this direction was made, when it was recognised that the expulsion of the α-particle causes the radio-element to change its position in the periodic table, not into the next family, but into the next but one in the direction of diminishing group number and diminishing atomic mass.[2] Last year doubtful points in the sequence of changes, consequent upon the branching of the disintegration series at the *C*-members, and on the existence, in uranium, of two chemically identical elements, uranium-*I* and -*II*, were cleared up, and the important step made that the *B*- and *C*-members of the three series exhibit identical electrochemical behaviour.[3] In the meantime, a systematic study of the chemical nature of those disintegration products not hitherto thoroughly studied from a chemical point of view had resulted in a remarkable extension of the feature which dominates the chemistry of the radio-elements.[4] Radioactinium was shown to be chemically identical with thorium; mesothorium-*II* with actinium; the three *B*-members and radium-*D* with lead; the three *C*-members and radium-*E* with bismuth; thorium-*D* and actinium-*D* with thallium[5]; and radium-*A* with polonium. Thus, not a single one of the radio-elements, known at the commencement of the year,

[1] *Ann. Report*, 1910, 285.

[2] F. Soddy, "Chemistry of the Radio-elements," 1911, p. 30.

[3] *Ann. Report*, 1912, 311, 321, 319. Compare also E. Marsden and R. H. Wilson, *Phil. Mag.*, 1913, [vi], **26**, 354; *A.*, ii, 907; P. Beer and K. Fajans, *Physikal. Zeitsch.*, 1913, **14**, 947; *A.*, ii, 907; A. B. Wood, *Phil. Mag.*, 1913, [vi], **26**, 586; *A.*, ii, 908; K. Fajans, *Physikal. Zeitsch.*, 1913, **14**, 951; *A.*, ii, 908; G. von Hevesy and L. von Putnoky, *Physikal. Zeitsch.*, 1913, **14**, 63; *Phil. Mag.*, 1913, [vi], **25**, 415; *A.*, ii, 175.

[4] A. Fleck, *Chem. News*, 1912, **106**, 128; 1913, **107**, 95; *T.*, 1913, **103**, 381, 1052.

[5] Compare also W. Metzener, *Ber.*, 1913, **46**, 979; *A.*, ii, 375.

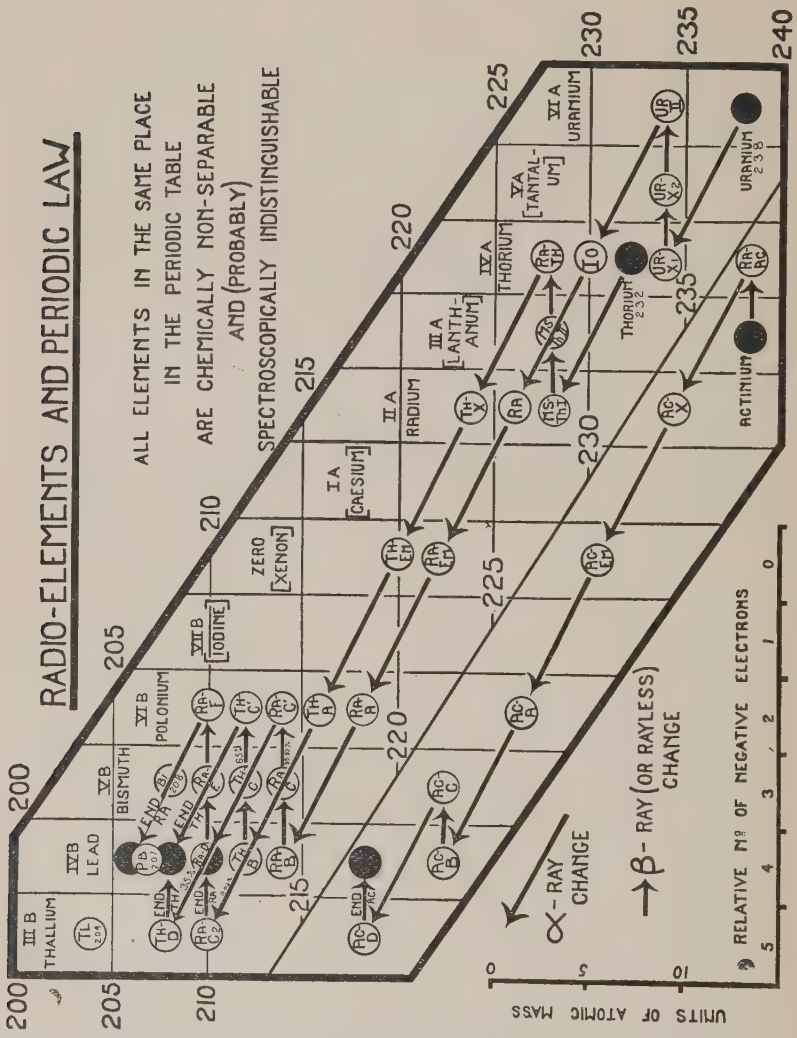
has a peculiar chemical nature unshared by others. All are chemically indistinguishable from one or other of the elements occupying the last twelve places of the periodic table, from thallium to uranium. With the sequence of changes fully elucidated and the chemical character of the majority of the radio-elements established, the α-ray rule was shown to hold generally, and, equally generally, a similar rule for the β-ray changes was found to apply. In the β-ray change, the element shifts its position in the periodic table in the opposite direction to that in the α-ray change, but into the next family, not into the next but one.[6] These two simple rules, consistently applied to the three disintegration series, constitute a sweeping generalisation connecting the chemical character of the radio-element, and the position it occupies in the periodic table with the kind of radioactive change in which it is produced. In addition to the purely chemical discoveries considered, an electrochemical examination of the radio-elements led independently to the same generalisation. It was found that the expulsion of the α-particle resulted in a product more electro-positive, and of a β-particle more electro-negative, than the parent.

The generalisation is illustrated in the chart (Fig. 1). This satisfactorily accounts for all the peculiar features that characterise the chemistry of the radio-elements. Whenever, by the expulsion of α- or β-rays, two or more elements come to occupy the same place in the periodic table, then, independently of all other considerations, such as the atomic weight, the disintegration series to which the element belongs, its radioactive character and the nature of the radioactive changes, in which it is produced, or by which it is transformed, these elements, occupying the same place, are non-separable from one another, and are, so far as is known, identical in chemical character. Each vertical row of the diagram consists of such a group of chemically identical elements. The ten occupied places contain over forty distinct elements, whereas if chemical analysis alone had been available for their separate recognition, only ten elements could have been distinguished. The places at the end of the periodic table, and probably elsewhere in the table, thus represent, not single homogeneous elements as has hitherto been supposed, but groups of elements identical in chemical character. To express this newly discovered complexity of matter, the terms "isotopic elements" or "isotopes" have been coined. Thus radiothorium, ionium, thorium, uranium-X_1, and radioactinium

[6] A. S. Russell, *Chem. News*, 1913, **107**, 49; *A.*, ii, 274; K. Fajans, *Physikal. Zeitsch.*, 1913, **14**, 131, 136; *Ber.*, 1913, **46**, 422; *A.*, ii, 276, 277; *Ber. Deut. physikal. Ges.*, 1913, **15**, 240; *A.*, ii, 493; *Le Radium*, 1913, **10**, 171; *A.*, ii, 660; F. Soddy, *Chem. News*, 1913, **107**, 97; *Jahrb. Radioaktiv. Elektronik*, 1913, **10**, 188; *A.*, ii, 275.

are a group of isotopic elements, the calculated atomic masses of which vary from 228 to 234. They all occupy the same place in

FIG. 1.



Reproduced by the courtesy of the British Association from a block illustrating "The Radio-elements and the Periodic Law," by F. Soddy, Section B, Birmingham, 1913.

the periodic table, and are chemically indistinguishable. This material identity, however, extends far beyond the chemical pro-

perties in the narrow sense, and embraces probably nearly all the common physical properties also, so that the experimental means capable of distinguishing and separating isotopes are very limited.[7] Thus, eleven years ago, the result that the radium and thorium emanation condense at practically the same temperature seemed very extraordinary. Now there is every reason to believe that isotopes will prove to be indistinguishable in volatility no less than in chemical properties. The question whether isotopes have the same spectrum, for example, was discussed for the case of ionium and thorium last year.[8] Important new evidence can be urged both for and against the general view. The recent generalisation that the magnitude of the atomic weight enters exactly into the series relationships of spectra, and the expectation that has been advanced that, ultimately, it should be possible to determine atomic weights from these series relationships more accurately than by chemical analysis,[9] is obviously opposed to the possibility that elements of different atomic masses can have the same spectra.

Neon and Metaneon.—On the other hand, what appears to be a case of isotopic elements outside the radioactive sequences has been discovered. As has been remarked, very few material properties depend directly on atomic mass. Fractional diffusion of gases is almost the only property that can be expected to effect a partial separation of a group of isotopic elements into their constituents. Whilst, to detect the non-homogeneity if it exists, the new positive ray method of Sir J. J. Thomson[10] is again almost the only one available. The examination of atmospheric neon by this method revealed the presence of atoms, in relatively small proportion, of mass 22, in addition to the known atom of mass 20. The relative proportion of the two kinds of atoms was unchanged after a prolonged fractionation of the gas by cold charcoal; but fractional diffusion showed that atmospheric neon is not homogeneous, and a partial separation, attested by a change of density, was effected by this means. No change in the spectrum corresponding with the change of density was observed, however, and the two elements appeared to be identical in all properties, except atomic weight.[11]

This accords with what has been found in the case of ionium

[7] "Chemistry of the Radio-elements. Part II. The Radio-elements and the Periodic Law." By F. Soddy: Longmans, Green & Co., 1914.

[8] *Ann. Report*, 1912, 321.

[9] W. M. Hicks, *Phil. Trans.*, 1913, A, **213**, 323; *A.*, ii, 810.

[10] Sir J. J. Thomson, Bakerian Lecture, *Proc. Roy. Soc.*, 1913, **89**, A, 1; *A.*, ii, 820.

[11] F. W. Ashton: Paper communicated to the British Association, Section A., Birmingham, 1913.

and thorium, as regards the spectra, and in the case of the radium and thorium emanation, as regards the volatility, and indicates that isotopes will prove to be identical in these respects as they are in chemical character. At the same time, the discovery is a most dramatic extension of what has been found for the elements at one extreme of the periodic table, to the case of an element at the other extreme, and strengthens the view that the complexity of matter in general is greater than the periodic law alone reveals. Although the complexity is greater, the problem of atomic structure has been much simplified, because the generalisation gives a probable explanation of the absence of exact simple numerical relations among the atomic weights.

Uranium-X_2 *or Brevium*.—When the rules were first applied there was one obvious lacuna between uranium-*X* and uranium-*II*, for, by the rules, two successive β-ray changes are necessary to shift an element in group IV into group VI. This suggested that uranium-*X* was probably complex, and that its two types of β-rays, one very hard and the other very soft, result in two successive changes, with the intervention of an intermediate element occupying the place in group V, hitherto vacant. The new element would be the homologue of tantalum. The resolution of uranium-*X* into two distinct radio-elements, named uranium-X_1 and uranium-X_2, followed almost immediately.[12] By application of the electrochemical rules, it was to be expected that uranium-X_2 would be more easy to separate electro-chemically than uranium-X_1, and it was found that polished lead plates, immersed for a minute in a feebly acid solution of uranium-*X*, gave the hard β-rays of uranium-*X*, which decayed with a half-period of 1·15 minutes. This corresponds with a period of average life for uranium-X_2 of 100 seconds, whereas the period of uranium-X_1, the parent, is 35·5 days. The chemical analogy of the new member to tantalum is clearly shown by other methods of separation. If uranium-*X*, separated from uranium, together with thorium, in acid solution, is added to an alkaline solution of potassium hexatantalate, uranium-X_2 is almost quantitatively precipitated with the tantalic acid, whilst uranium-X_1 remains in solution with the thorium. Similarly, the separation may be effected by filtering the uranium-*X* solution through a layer of moist tantalic acid. By this and many other reactions it was proved that uranium-X_1, of average period 35·5 days, emits only the soft β-rays and produces uranium-X_2, of average period about 1·6 minutes, which emits the hard β-rays.

[12] K. Fajans and O. Göhring, *Naturwissenschaften*, 1913, **1**, 339; *Physikal. Zeitsch.*, 1913, **14**, 877; *A.*, ii, 909; O. Hahn and L. Meitner, *ibid.*, 758; *A.*, ii, 821; A. Fleck, *Phil. Mag.*, 1913, [vi], **26**, 528.

Although uranium-X_2 is chemically analogous to tantalum, it should prove to be separable from it, just as radium is from barium, or polonium is from tellurium. As it is a new chemical type, its discoverers have given it the distinctive name "Brevium." At present it is unique among the radio-elements, in occupying a place in the periodic table by itself. This distinction is, however, likely to be only temporary, as already it is necessary to postulate as isotope to account for the origin of actinium.

Origin of Actinium.—The unsolved problem of the origin of actinium has been considerably narrowed down by the periodic law generalisation. Being in group III, its parent must be in group V, isotopic with brevium, if it is formed in an α-ray change, or in group II, isotopic with radium, if it is formed in a β-ray change. As radium is the only member of the uranium series in group II, the latter alternative is equivalent to supposing that radium itself is the parent—that, in addition to the α-ray change into the emanation, radium suffers a branch β-ray change into actinium. Although this is supported by the fact that radium, and also thorium-X, in the same place, give, in addition to α-rays, some soft β-rays, which constitute something of an exception to the simple rules, the production of actinium from radium has been disproved.[13] No detectable amount of actinium was found in a preparation of radium bromide which had been kept for ten years without interference, and contained 13·2 mg. of radium (element). Were actinium the direct product of radium, this negative result would mean that the period of actinium must be at least fifteen million years, whereas it is practically certain that its period cannot be as great as one hundred years.

The alternative is to suppose that actinium results from an element in group V by an α-ray change, and, since brevium is short-lived and gives no α-rays, this requires that an unknown isotope must exist in the uranium series. The suggestion has been made that the series may branch at uranium-X_1, β-rays being expelled in both branches, so that two isotopic products result.[14] The branchings so far studied have been of the character that in one mode a β-ray change is followed by an α-ray change, and, in the other mode, an α-ray change is followed by a β-ray change. The suggestion that in both branches the same type of ray is expelled is novel, and although not necessarily improbable, would, if adopted, largely increase the number of possibilities to be taken into account. One, in particular, seems worth discussion.

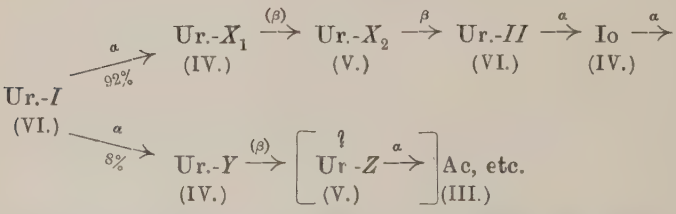
Uranium-Y.—In 1911 Antonoff found that the soft β-radiation

[13] F. Soddy, *Nature*, 1913, **91**, 634.

[14] O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1913, **14**, 752; *A.*, ii, 821.

of uranium-X decays, in certain cases, abnormally rapidly for the first few days after the separation of the substance from uranium, and concluded that there exists in the series a branch product, uranium-Y, similar in chemical properties to, but not identical with, uranium-X, of half-period 1·5 days, giving soft β-rays similar to those given by uranium-X_1, as we now know.[15] This observation has been called in question, but repeated and reaffirmed by the original discoverer,[16] who states that the proportion of radiation contributed by uranium-Y is of the order to be expected if it is the starting point of the branch actinium series. This has now been independently confirmed.[17] Not only has the abnormal decay curve of uranium-X been obtained, but also some evidence of a corresponding abnormality in the recovery curve of pure uranium preparations, both quite in keeping with the view that of the total soft β-radiation of uranium-X, some 8 or 10 per cent., is produced by a separate product of much shorter period, uranium-Y. However, uranium-Y appears from this work to be not merely chemically similar to, but identical or isotopic with uranium-X_1. Whether or no the effects are obtained depends not at all on the particular chemical separation adopted, but only on the time of accumulation of the products before separation. The shorter this is, the greater is the small proportion of the effect due to the shorter-lived minor branch product. This probably accounts for the difficulty experienced by others in confirming the work. The direct production of two isotopes from one of the two uraniums indicates branching of the series by two simultaneous changes, in both of which α-rays are expelled, as shown in Fig. 2.

FIG. 2.



It will be observed that there is still a missing member, called uranium-Z in the figure, to be found, which should be isotopic with uranium-X_2, and should give actinium as the direct product in an α-ray change. But whether the branch occurs, as shown, at the first member, uranium-I, or at the fourth member, uranium-II, would be

[15] *Ann. Report*, 1911, 288.

[16] A. Fleck, *Phil. Mag.*, 1913, [vi], **25**, 710; *A.*, ii, 464; G. N. Antonoff, *ibid.*, 1913, [vi], **26**, 1058; *A.*, 1914, ii, 17.

[17] F. Soddy, *ibid.*, 1914, [vi], **27**, 215.

experimentally indistinguishable, save by indirect methods, such as the determination of the atomic weight of actinium and its products. The scheme shown would make the atomic weight of actinium 230, whereas the alternative would make it 226, identical with that of radium.

A generalisation in this field favours the latter alternative.[18] As a rule, in any group of isotopes, the α-ray giving members are the more stable the higher the atomic weights, and the β-ray giving members are the more stable the lower the atomic weight. Thus, in the thorium group, the order of increasing stability and atomic weight among the α-ray members is: radiothorium (2·9 years, 228), ionium (100,000 years, 230), thorium (4×10^{10} years, 232). Since radioactinium is the least stable of all in this group, its atomic weight ought to be less than 228. From this generalisation the atomic weights of actinium and its products generally appear to be similar to that of radium and its products. The generalisation does not hold without exception, the most notable being polonium, which at once is the most stable and has the smallest atomic mass of the six α-ray giving members of this isotopic group.

Nature of the End-Products.—The connexion between the changes and the properties of the products enables the place occupied, and the whole chemical character of those members, to be predicted without uncertainty, in the case where, either by reason of excessive instability—the *A*- and *C'*-members—or excessive stability—the end-products—the elements are outside the range of experimental investigation. Hitherto there has been a general belief that the end product of radium was lead, but there was no evidence whatever as to the nature of the end-products of actinium and thorium. Fig. 1 shows that *all* the five end-products fall into the same place, and must be the isotopes of lead. The calculated atomic weights of the two end-products of the thorium series are the same, namely, about 208, and that of the main end-product of uranium is 206, whereas in the international list the atomic weight of lead figures as 207·1. This raises directly the question of the homogeneity of lead, for if it were a mixture of the end-products of uranium and thorium in similar proportion, the atomic weight would be about that actually found. On the other hand, if the generalisation of Fajans holds good, it is to be expected that the stability of these various isotopes will be connected with their atomic weight. If, for example, the two supposed end-products of the thorium series, like the corresponding product, radium-*D*, expelled a β-particle in further very slow changes, the product

[18] K. Fajans, *Le Radium*, 1913, **10**, 171; *A.*, ii, 660; *Physikal. Zeitsch.*, 1913, **14**, 951; *A.*, ii, 908.

would be, in chemical character and atomic weight, the same as bismuth; but as in the formation of these two products from the original parent substances different energies have been lost, the two isotopic bismuths so formed would not be identical, and one of them might further expel an α-particle to give thallium (204), for both bismuth and thallium occur in radioactive minerals. This, of course, is a pure speculation. The interesting point is that, in stability, the supposed end-products of the thorium series should be intermediate between radium-*D* and radium-*G*, and, therefore, might not be sufficiently stable to accumulate in minerals and to constitute a perceptible fraction of the lead occurring therein. So that, although the atomic weight of lead, from radioactive sources as different as possible in regard to uranium and thorium content and geological horizon, should be re-examined, it by no means necessarily follows that any difference in atomic weight will be found.

Branching of the Actinium Series.—The earlier observation, which made it appear that actinium-*C* gave out two types of α-rays, like thorium-*C*, but unlike in possessing ranges nearly the same,[19] has not been confirmed. In Fig. 1 the actinium series is represented as unbranched at the *C*-member. Without prejudice to this point, it appears certain that, if not the whole, at least very nearly the whole, of the actinium-*C* atoms disintegrate by the α-ray mode, and what is, in this series, overwhelmingly the main branch is the minor branch in both the radium and thorium series. Recently some evidence of a branching has been obtained, precisely analogous to that which occurs in the other two series.[20]

In addition to the α-rays, from actinium-*C*, of range 5·12 cm. in air at N.T.P., about one in 600 have been found of longer range, 6·1 cm. This is very nearly the range of the α-rays of actinium-*A*. It must be remembered that recoiled actinium-*X* is always present in the active deposit of actinium, as ordinarily prepared,[21] so that further discussion may be postponed.

The Structure of the Atom.

On Rutherford's theory of atomic structure,[22] which was put forward to account for "single scattering"—that is, for the large angles through which a very small proportion of the α-particles are deflected in their passage through matter, by rare, exceptionally close, single encounters with atoms—the mass of the atom, in association with positive electricity, about one unit of

[19] *Ann. Report*, 1909, 236.
[20] E. Marsden and R. H. Wilson, *Nature*, 1913, **92**, 29.
[21] *Ann. Report*, 1906, 363; 1907, 328; 1909, 246.
[22] *Ibid.*, 1911, 273.

charge per two units of mass, occupies a single central nucleus of excessively minute dimensions, in diameter only one ten-thousandth of the atomic diameter. Around this nucleus a number of negative electrons, equal to the value of the positive nuclear charge, circulate as an outer ring or shell. This atom is, of course, not stable according to ordinary electro-dynamical laws, for nothing apparently operates to prevent the dispersion of the extremely concentrated central positive charge, but it is now recognised that these laws require modification. The model has been used with very considerable success, in conjunction with Planck's theory of quanta, and leads to results, in connexion, for example, with the series relationships of the hydrogen and helium spectra, in striking accord with experimental determinations.[23]

It now appears that the magnitude of this central positive charge, in terms of the unit atomic charge, for example, that carried by the hydrogen ion, is probably the same as what is conveniently termed the "atomic number."[24] The atomic number is the number of the place an element occupies in the periodic table, when the successive places from hydrogen to uranium are numbered in sequence, hydrogen being unity, helium two, lithium three, and so on. If the eleven known representatives of the rare-earth group, between cerium and tantalum, exclusive, are all that exist, the atomic number for uranium would be 89. As regards the relative value of the nuclear charge, and its variation by units in passing from one place to the next of the periodic table, Fig. 1 shows this clearly. The α-particle carries two positive atomic charges, and its expulsion causes the element to move two places in the table, that is, diminishes the atomic number by two. The β-particle is an atom of negative electricity, and its expulsion causes the element to alter its place by one in the opposite direction, that is, causes the atomic number to increase by one, whereas the successive expulsion of two β- and one α-particle in any order brings the element to the same place and with the same atomic number, therefore, as initially.

The only assumption made is that both the α- and β-particles are expelled from the central nucleus, not from the outer ring. This is in accord with the view, everywhere accepted, that radioactive changes are much more fundamental in character than any other known changes, and concern a region of the atom not affected in ordinary chemical and physical changes. As, on the theory, the mass of the atom is concentrated in the nucleus, and the

[23] N. Bohr, *Phil. Mag.*, 1913, [vi], **26**, 1, 476, 857.

[24] A. van den Broek, *Nature*, 1913, **93**, 373, 476; F. Soddy, *ibid.*, 399, 452; E. Rutherford, *ibid.*, 423.

α-particle constitutes an appreciable part of the atomic mass, there can be little doubt that the α-particles have their origin in the nucleus. With regard to the β-particles, something like a direct proof has been obtained. If the β-particles came from the outer ring and were the same electrons as are concerned in electrochemical changes of valency, the loss of two β-particles by uranium-X_1 in the formation of uranium-*II* should be equivalent to the loss of two electrons by uranous salts in their electrochemical oxidation to uranyl salts, and uranium in uranous salts should be isotopic with thorium. Uranous and thorium salts are very similar in chemical character, but a recent examination shows that they are readily separable from one another by chemical methods.[25] Hence the positively charged nucleus of the atom must contain some negative electrons—at least six in the case of uranium to account for the six β-rays expelled during the disintegration—which are to be distinguished from the electrons in the outer shell. If the mass of the uranium atom were due entirely to potential α-particles or the nuclei of helium atoms, for which unit charge corresponds with two units of mass, there would be about thirty nuclear electrons to give 89 as the atomic number, whereas if, as has been surmised, the hydrogen nucleus were a second constituent of the nuclear structure, more must be postulated, as in this case unit mass goes with unit charge. It is the difference between positive and negative charges which gives the atomic number or the position of the element in the periodic table. Isotopes are elements for which the algebraic sum of opposite charges is the same, but the arithmetical sum is different.

The surprising results in crystallography and chemistry following upon the discovery that the *X*-rays are regularly reflected by crystals[26] are discussed in the report on Mineralogical Chemistry. Equally remarkable are the results in the field under discussion, for the property has enabled the wave-length of the *X*-rays, which is the order of ten thousand times smaller than that of visible light, to be determined. Each element gives a homogeneous characteristic *X*-radiation, and the wave-length of this characteristic radiation, equally with the wave-lengths of the luminous spectrum, is connected, by Bohr's theory, with the magnitude of the nuclear charge. The series of metallic elements from calcium to zinc in the periodic table, for which the atomic numbers extend from 20 to 30, were all in turn, excepting scandium, made the anticathode of an *X*-ray tube, and the spectrum in each case was found, by reflection from a crystal surface, to consist of two lines only, one strong and one weak. The wave-length of the stronger

[25] A. Fleck, *T.*, 1914, **105**, 247. [26] *Ann. Report*, 1912, 302.

lines corresponded with the atomic numbers 19 to 29, showing unit difference of nuclear charge from place to place. What will be one of the most interesting points to chemists is that the nuclear charge increases in the order: iron, cobalt, nickel, which is the order the elements should be placed in the periodic table, and not in the order of the atomic weights: iron, nickel, cobalt. This is a definite proof that the "exceptions" to the sequence of atomic weights in the periodic table are real, and not due to erroneous determinations.[27] Much remains, obviously, to be worked out in this new field, but the results attained are sufficient to demonstrate how many novel methods of surprising power are converging simultaneously on the outstanding problem of the structure of atoms.

Behaviour of Radio-elements in Solution, and to Solvents.

Advantage has been taken of the fact that none of the known cations differ widely in mobility, and that the diffusion coefficient, in the presence of great excess of anion, varies inversely as the valency, in order to determine the valency of the radio-elements from diffusion experiments.[28] The first series of determinations gave results for the valency in accord with the chemical character for those radio-elements which had already been placed in the periodic table. Radium-*E* and the *C*-members, however, appeared to act as bivalent, and the *B*-members as univalent, when first determined by this method, in apparent disagreement with the isotopism of these elements to bismuth and lead respectively, as shown by the chemical examination published at about the same time. Later a re-examination gave values in accordance with the chemical evidence.[29] It was shown that, for example, thorium-*B* in certain circumstances acts as a univalent ion in the same way as lead does in the ion $PbCl^+$.

The chemical identity of isotopes has been extended to include the electro-chemical behaviour. The decomposition voltage curves for thorium-*C* and radium-*E* are the same as that of bismuth, and for thorium-*B* as that of lead. In addition thorium-*B* may be deposited on the anode under the same conditions as lead in the form of peroxide.[30] By the use of these radioactive substances as indicators, the behaviour of lead and bismuth for electrode potentials lying above the decomposition voltage has been studied. In the electro-deposition of radio-elements, the electrode potential is of the first importance. The passage of the current, and hence the

[27] H. G. J. Moseley, *Phil. Mag.*, 1913, [vi], **26**, 1024.
[28] G. von Hevesy, *Physikal. Zeitsch.*, 1913, **14**, 49; *A.*, ii, 174.
[29] *Idem. ibid.*, 1913, **14**, 1202; *A.*, 1914, ii, 16.
[30] F. Paneth and G. von Hevesy, *Monatsh.*, 1913, **34**, 1593; *A.*, ii, 1009.

difference between anode and cathode are entirely secondary. In practical electrochemical separations of one radio-element from another the addition of a perceptible amount of the isotope of the element it is not desired to separate is recommended. For example, in separating the *B*-members from the *C*-members, addition of lead hinders the deposition of the former, and results in a purer preparation of the *C*-member. An extended attempt to alter the concentration of radium-*D* to lead in a mixture by fractionation was unsuccessful. About twenty different methods failed to affect the least change in concentration.[31] This identity of behaviour has been made use of in the determination of the solubility of the excessively insoluble compounds of lead, such as the chromate and sulphide. To the lead is added a quantity of radium-*D*, infinitesimal in amount, but, after the formation of the products radium-*E* and -*F*, possessing intense radioactivity. The activity of the evaporated saturated solution of the insoluble lead compound enables the amount of lead present to be estimated, though this is analytically undetectable. In this way, the solubility of lead chromate in water at 25° was found to be 0·012 milligram per litre, and of lead sulphide, 0·3 milligram in water and 0·15 milligram in a saturated solution of hydrogen sulphide. Similar experiments could be carried out with thorium, radium, or bismuth, using ionium, thorium-*X*, or radium-*E*, respectively, as indicators. The possibilities of the method are very numerous.[32]

Two lines of work indicate that the radio-elements, although present in such infinitesimal concentrations, often behave in solutions as colloids rather than as electrolytes. Thus polonium may be separated from lead, radium-*D* and -*E*, by dialysing the solution through animal membranes, or thin parchment paper. The polonium remains behind in the cell in a pure condition.[33]

This may be used to effect the separation, but on a large scale the process recommended is the crystallisation of the hot saturated solution of the radio-lead nitrate solution, and electrolysis of the mother liquor, after addition of a little bismuth, between platinum electrodes, with a cathode potential not exceeding 0·08 volt, or current strength 0·16 milliampere per sq. cm. The polonium is removed from the electrodes by volatilisation at 1000°. The vapour condenses preferably on palladium or platinum, especially the former, rather than on other metals or on quartz, and so may be concentrated.[34]

[31] F. Paneth and G. von Hevesy, *Monatsh.*, 1913, **34**, 1393; *A.*, ii, 1008.

[32] *Idem. ibid.*, 1913, **34**, 1401; *A.*, ii, 1075; and G. von Hevesy, British Association, paper read before Section B, Birmingham, 1913.

[33] F. Paneth, *Monatsh.*, 1913, **34**, 401; *A.*, ii, 273.

[34] F. Paneth and G. von Hevesy, *Monatsh.*, 1913, **34**, 1605; *A.*, ii, 1011.

In acid solution, all the radio-elements dialyse normally as crystalloids; in neutral solution the velocity of dialysis in the case of polonium and radium-*E*, and in ammoniacal solution in the case of thorium-*B* also, is very much reduced. The diffusion-coefficients in acid, neutral and alkaline solutions of these elements bear out the conclusions drawn from the results of dialysis. The change from crystalloid to colloid is accompanied by a change of sign of the charge carried by the particles, the colloidal particles now migrating to the anode in an electric field. In a condition where both forms of the same radio-element exist together in solution, the migration of the ions to the cathode is not prevented, but only hindered, by the insertion of a parchment membrane, but the migration of the colloid particles to the anode is almost completely prevented by the membrane. The size of the colloidal particle is probably very small, and it consists of an aggregation of but few atoms compared with ordinary colloidal particles. It is altogether beyond the range of the ultra-microscope. This is to be expected in view of the excessively attenuated concentrations. When it is remembered that in none of these cases is the solution a saturated one, and, even for the most insoluble, the solubility product of the ions is very far from being approached, it is clear that the aggregation cannot be due to purely physical causes, but that some unknown chemical or adsorption phenomena are involved. Zsigmondy has suggested that the colloidal particles may be formed by the adsorption of the radio-element by existing colloid particles, such as aluminium hydroxide or silica, derived from the materials of the containing vessels. This explanation necessitates the specific adsorption by the colloid particles of some of the radio-elements, and not of others. A closer examination of the adsorption phenomena of the radio-elements is therefore called for. Along these lines may be expected an explanation of the very inexplicable fact that the radio-elements show such definite analytical and chemical reactions at such infinitesimal concentrations.[34a]

In the other research, it was found that the ratio of cathode to anode activity, obtained by the electrolysis of water containing dissolved radium emanation, could be varied in the proportion of 40,000 to 1 in a manner impossible to account for if the products, radium-*A*, -*B*, and -*C* existed as ions, but completely in accord with predictions made from the theory of colloids. In pure water, the *A*-member is deposited on the anode, the *B*-member on the cathode, and the *C*-member on both electrodes, and the view taken is that the *A*-member exists as a positive hydrosol, the *B*-member

[34a] F. Paneth, *Kolloid. Zeitsch.*, 1913, **13**, 1, 297; *A.*, ii, 747; 1914, ii, 19; K. Fajans and P. Beer, *Ber.*, 1913, **46**, 3486; *A.*, ii, 1010.

as a negative hydrosol, and the *C*-member in both forms. The addition of acids containing hydrion, or much more powerfully, of a multivalent cation such as that of aluminium, stabilises the positive hydrosol, whilst it neutralises and ultimately reverses the sign of the negative hydrosol. Basic ions, such as hydroxyl, or the citric acid anion, act in the opposite manner. In this way the deposition on either electrode may be suppressed, and that on the other accentuated. The transport of the products by the current is regarded as being due to electrophoresis rather than to electrolysis.[35]

An interesting series of experiments on the solubility of the active deposit of radium deposited from the emanation on surfaces of glass and metals, showed that from a glass surface only one-half of the active deposit is removed by boiling with acids, whereas with gold and platinum surfaces the soluble part is greater.[36]

There is little doubt that the recoil of the atom of radium-*B* in its production from radium-*A* must drive one-half of it to a perceptible depth beneath the surface, where it is protected from the attack of solvents. With radium-*B* deposited on a second plate, by recoil from the first, the whole is soluble. In organic solvents, especially carbon disulphide, radium-*A* is soluble, whereas the other two members are nearly insoluble. This is in accord with the position of radium-*A* in the sulphur family. When the active deposit is formed on plates of gold and platinum, which have been previously saturated electrolytically with hydrogen and oxygen respectively, it was found that oxygen diminishes the solubility, especially of radium-*C*, whilst hydrogen diminishes that of radium-*A*. It will be recalled that in oxygen the volatility of radium-*C* occurs at a very much higher temperature than in hydrogen.[37] The formula of Arrhenius for the variation of velocity of solution of metals in acids with temperature has been tested for the radium active deposit, and has been found to hold approximately. A similar series of experiments with the active deposit of thorium showed that thorium-*B* is dissolved more quickly than thorium-*C* by water, salt solutions, alkalis and acids, but less quickly by organic solvents.[38]

Radium.

Atomic Weight.—The value found for the atomic weight of radium by analysis of the chloride,[39] 225·95, was confirmed by

[35] T. Godlewski, *Le Radium*, 1913, **10**, 250; *A.*, ii, 1011.
[36] E. Ramstedt, *ibid*, 159; *A.*, ii, 659.
[37] *Ann. Report*, 1912, 318.
[38] C. F. Hogley, *Phil. Mag.*, 1913, [vi], **25**, 330; *A.*, ii, 273.
[39] Compare *Ann. Report*, 1912, 289.

converting the material into the bromide, and fractionally crystallising it numerous times. The value found in one set of determinations from the ratio $RaBr_2/AgBr$ was 225·96, and in another, from the ratio $RaBr_2/Ag$, 225·97. A spectroscopic examination of the final product showed no trace of barium. In the mother liquors, barium was detected, and its quantity estimated as 0·03 per cent. From this it is calculated that in the preparations used the percentage of barium in the chloride could not exceed 0·004, and in the bromide 0·002, which is insufficient to affect the accuracy of the atomic-weight determinations. A similar degree of purity may be assumed for the International Standard, so that, before the barium can cause any error, the radioactive methods of comparing standards must be increased in accuracy a hundredfold.[40] The atomic weight being so near the whole number suggests that the atomic weight of uranium should be very nearly 238 instead of 238·5, as in the international list, if mass is conserved in radioactive changes.

Valency.—The bivalency of radium has been shown by a new method, depending on the volume of liquid transported in a capillary tube by electric endosmose, under the application of considerable electric potentials. The interest of the method consists in the excessively minute amounts, 0·01 to 0·001 milligram of substance required.[41]

Estimation.—A method for the rapid estimation of radium by the emanation method depends on the use of a micro-furnace, in which a tiny fragment of the mineral is heated for a few seconds to 2000° or 3000° in a cavity in a thin carbon rod, inside a small chamber provided with a rubber balloon to allow for expansion. Rapid escape of emanation commences at 750°, and is complete at bright redness.[42]

Technical Extraction.—The reduction of the radiferous "raw sulphates" has been effected by mixing the absolutely dry, finely powdered material with finely powdered calcium hydride, and firing the mass with magnesium ribbon and a priming mixture, as in the thermite reaction. The reduction is complete in a few minutes, and the product is leached out with acid as quickly as possible to avoid oxidation of the sulphides with air.[43] It may be doubted whether such a reaction could be technically advantageous on account of the high cost of the reducing agent.

[40] O. Hönigschmid, *Monatsh.*, 1913, **34**, 283 ; E. Haschek and O. Hönigschmid, *ibid.*, 351 ; *A.*, ii, 268 ; S. Meyer, *Physikal. Zeitsch.*, 1913, **14**, 124 ; *A.*, ii, 267.

[41] H. Freundlich and G. von Elissafoff, *Physikal. Zeitsch.*, 1913, **14**, 1052 ; *A.*, ii, 1008.

[42] A. L. Fletcher, *Phil. Mag.*, 1913, [vi], **26**, 674 ; *A.*, ii, 904.

[43] E. Ebler and W. Bender, *Zeitsch. anorg. Chem.*, 1913, **83**, 149 ; *A.*, ii, 904.

Uranium–Radium Ratio.—A new determination of the ratio of radium to uranium in a variety of minerals, in which the uranium was estimated chemically and the radium by both the emanation and γ-ray methods, by the use of standards checked against the international standard, gives the value $3{\cdot}328 \times 10^{-7}$.[44] A review of all the evidence available by which the periods of uranium and radium may be calculated has shown that the different methods lead to substantial agreement, and that the half-periods, respectively, are 5×10^9 and 1730 years, corresponding with the average-life periods, $7{\cdot}25 \times 10^9$ and 2500 years.[45] The half-periods for thorium and uranium, calculated from the range of the α-particle and the ionisation per unit weight, have been independently found to be $1{\cdot}8 \times 10^{10}$ and 5×10^9 years.[46]

Various.—The effect of very low temperatures on the penetrating radiation from radium has been carefully studied. Immersion for 1·5 hours in liquid hydrogen did not produce any variation attaining 0·1 per cent., and probably not 0·02 per cent.[47] By an ingenious application of the principle of the radium-clock, in which the negative charge, carried by the penetrating rays, is used to charge a tube containing radium positively, very high potentials have been obtained. A tube of radium emanation was suspended by an insulating support in a high vacuum, and the potential it attained measured by a simple form of attracted disk electrometer. The tube quickly charged itself to a high potential. In spite of all precautions to obtain as perfect a vacuum as possible, the attainable potential was limited to a maximum of about 150,000 volts, at which a discharge always occurred.[48]

The Actinium Series.

Period of Actinium-X.—A small change has to be recorded in the period of actinium-*X*, which still, however, remains an exception to the Geiger-Nuttall relation, the earlier reported resolution of radioactinium into two products having been withdrawn.[49] From β-ray measurements, the half-period of actinium-*X*, very carefully purified, was found to be 11·6 days, corresponding with the average life period, 16·8 days. For radioactinium the accepted values were

[44] B. Heimann and W. Marckwald, *Physikal. Zeitsch.*, 1913, **14**, 303; *Jahrb. Radioakt. Elektronik*, 1913, **10**, 299; *A.*, ii, 374.

[45] S. Meyer, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, (iia), 1087.

[46] H. N. McCoy, *Physical Review*, 1913, 1, 393.

[47] Mme. M. Curie and H. K. Onnes, *Le Radium*, 1913, **10**, 181; *A.*, ii, 746.

[48] H. G. J. Moseley, *Proc. Roy. Soc.*, 1913, A, **88**, 471.

[49] *Ann. Report*, 1912, 294; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1913, **14**, 752; *A.*, ii, 821; A. S. Russell and J. Chadwick, *Phil. Mag.*, 1914, [vi], **27**, 112.

confirmed (19·5 and 28·2 days).[50] No β-radiation could be detected from the very carefully purified actinium. In another determination, by α-ray measurements, the value 11·35 days for the half-period of actinium-*X* was obtained.[51]

α-Rays.

Experiments on the scattering of the α-rays by gases[52] and metal foils[53] have been continued, with results in agreement with the requirements of Rutherford's theory of the structure of the atom (p. 270). The theory has been quantitatively tested, as regards the variation of the number of α-particles deflected when (1) the angle of scattering, (2) the thickness of the foil, (3) the atomic weight of the scattering material, and (4) the velocity of the α-rays are varied. Although the results are approximately in agreement with the view that the positive nuclear charge is one-half of the atomic weight, it is probable that they would be more perfectly in agreement with van den Broek's view that the charge is equal to the atomic number, which for heavy elements is somewhat less than half the atomic weight.

Attention may be directed to a comparison of the ranges of the α-rays of radium-*C* and polonium in hydrogen and helium respectively,[54] since this is, theoretically, a very interesting case of a denser gas allowing the α-particles to travel in it slightly further than in a lighter gas. The ranges of the α-ray of radium-*C* in the two gases at N.T.P. are, respectively, 29·36 cm. in hydrogen, and 30·84 cm. in helium. This furnishes the simplest possible proof, as previously pointed out, of the monatomicity of the helium molecule. For, on Bragg's law, the atomic stopping power is approximately proportional to the square root of the atomic weight. If the helium molecule is monatomic, the number of atoms in the path of the α-ray will be twice as great in hydrogen as in helium, and the stopping power of each atom twice as great in helium as in hydrogen, whereas any other assumption must make the range in helium less than in hydrogen.

Pleochroic Haloes.—An attempt has been made to arrive at the age of the pleochroic haloes occurring in the mica of Haughtonite, co. Carlow, which contains no thorium haloes, but numerous uranium haloes of all stages of development, from the smallest, due

[50] O. Hahn and M. Rothenbach, *Physikal. Zeitsch.*, 1913, **14**, 409 ; *A.*, ii, 463.
[51] H. N. McCoy and E. D. Leman, *ibid.*, 1280 ; *A.*, 1914, ii, 17.
[52] E. Rutherford and J. M. Nuttall, *Phil. Mag.*, 1913, [vi], **26**, 702 ; *A.*, ii, 898.
[53] H. Geiger and E. Marsden, *ibid.*, 1913, [vi], **25**, 604 ; *A.*, ii, 371.
[54] T. S. Taylor, *ibid.*, 1913, [vi], **26**, 402 ; *A.*, ii, 899.

to the rays of uranium and ionium only, to the largest due to the fully darkened haloes, completed to the range of the α-rays of radium-*C*.[55] The number of α-particles required to produce a certain density of staining in the mica was experimentally determined, the mass of the nucleus giving the halo was estimated microscopically from its dimensions, and the quantity of radium per unit of mass assumed from analogy to the radium content of large zircons and cyrtolite. The last is, of course, the uncertain factor, and the results were dealt with in all cases to yield the lower limit possible for the age. The results are interesting in that they confirm the somewhat excessive periods of age given by the helium and lead contents of uranium minerals. The haloes may most safely be regarded as of early Devonian age, and the results point to a period of not less than four hundred million years as being required in their formation.

β-Rays.

The analysis of the slower β-rays given by radium-*B* and radium-*D* showed in each case four distinct beams of velocity, in terms of that of light, 0·361, 0·362, 0·412, 0·422 for the first, and 0·342, 0·344, 0·390, and 0·402, for the second substance. The differences between the energies of the several groups of rays are the same for each substance, within the error of measurement. This leads to the conclusion that in each case the rays are produced by the same mechanism.[56] Taken in combination with the isotopism of the two substances, the result is very suggestive. An exhaustive analysis has been made of the very complex β-radiations of radium-*B* + *C*, from photographs taken by a new method, which enables a comparatively wide slit to be employed without loss of sharpness.[57] The velocity and energy for 16 lines from radium-*B* and 48 lines from radium-*C* have been tabulated.

With regard to radium-*B*, no lines were observed with a velocity above 0·832, although it is probable that faster beams exist which are masked by the stronger lines of radium-*C*. The slowest line observed had a velocity of 0·365. Two complex groups of low velocity lines shown strongly by radium-*B* were shown faintly by radium-*C*. For radium-*C* 29 lines were observed over the range of velocity from 0·9858 to 0·946, the energy of which were all integral multiples of $E(=0{\cdot}428\times10^{13}e)$. The integers were the alternate odd integers from 59 to 47, and, with the exception of 45, every

[55] *Ann. Report*, 1910, 260; J. Joly and E. Rutherford, *Phil. Mag.*, 1913, [vi], **25**, 644.

[56] J. Danysz, *Le Radium*, 1913, **10**, 4; *A.*, ii, 270.

[57] E. Rutherford and H. Robinson, *Phil. Mag.*, 1913, [vi], **26**, 717; *A.*, ii, 899.

integer between 46 and 24. Below this, the differences of energy between the lines were much smaller, and the plates were crowded with fine lines extending right into the low velocity regions where radium-*B* shows strong lines. No simple relation appears to hold between the energies of the radium-*B* lines. This is probably connected with the fact that whereas the γ-radiation from radium-*C* is homogeneous, that from radium-*B* consists of three widely-different types. The quantity *E* represents, on Rutherford's theory of the origin of γ-rays, the energy abstracted from the β-particle in passing through certain regions of the atom and converted into γ-ray energy.

There is one point of interest in connexion with the expulsion of α-rays. In the cases most closely studied the recoil product also carries a single positive charge,[58] so that three positive charges result. Two of these are accounted for by internal compensation within the atom, the outward sign of which is the shift of two places in the periodic table. The third is not yet accounted for. An attempt to detect the expulsion of a soft β-ray from radium-*A* led to no result.[59] It is quite possible, however, that the third positive charge may be compensated for by the loss of a δ-ray, which would not be detectable in ordinary circumstances. Radium,[60] thorium-*X*, and radioactinium do give soft β-rays in addition to α-rays, and only the latter are accounted for in the change of place in the periodic table. On the other hand, the two rayless changes, of mesothorium-*I* and actinium, are equivalent to β-ray changes in the alteration of place they produce. These points, which are of the nature of exceptions to the simple generalisation, call for fuller examination.

γ-Rays.

The chief centre of interest in the physical examination of the various types of rays has been successively, first the α-rays, then the β-rays, and now the γ-rays. On the one hand, the view has triumphed that the γ-radiation is essentially homogeneous. This view was put forward after the exhaustive examination of the γ-rays of radium in various materials, from a thickness equivalent to 1 cm. of lead up to 22 cm. A repetition with larger quantities of radium, in which mercury was used as the absorbent, showed a strictly exponential absorption between the thickness of from 1 to 22·5 cm. The value found for μ/d, the absorption-coefficient

[58] *Ann. Report*, 1910, 272; H. P. Walmsley, *Phil. Mag.*, 1913, [vi], **26**, 401; *A.*, ii, 905.

[59] W. Makower and S. Russ, *Proc. London Phys. Soc.*, 1913, **25**, 253; *A.*, ii, 654.

[60] Compare L. Kolowrat, *Le Radium*, 1913, **10**, 280.

divided by the density, was $4{\cdot}38 \times 10^{-2}(\text{cm.})^{-1}$, in almost absolute agreement with the former value found for lead.[61] No evidence of an ionising radiation more penetrating than the known γ-rays was obtained. Through 30 cm. of mercury it can be calculated that no radiation could be detected, even from 10 grams of radium, so that it would be thought that the equivalent of the 76 cm. which surrounds us as an atmosphere must screen us absolutely from any cosmical source of γ-rays that exists (p. 288).

On the other hand, the departure of the absorption curves from the simple exponential type, for small thicknesses of material, has been shown to be due to the existence of a large number of types of homogeneous γ-radiation, varying in penetrating power from those of thorium-*D*, for which μ/d is $3{\cdot}5 \times 10^{-2}(\text{cm.})^{-1}$, to one of the types given by radium-*B*, for which μ/d is 85, which are hardly more penetrating than α-rays.[62] So that, just as in the case of the β-rays, fuller examination has shown that the most obvious more penetrating types are by no means the only ones that exist. Twenty types have so far been distinguished, as set forth with the values of μ/d in aluminium for each type, in the following table:

Element.	At. wt.	μ/d (Al).	Element.	At. wt.	μ/d (Al).
Radium-*B*	214	85·0 14·7 0·188	Thorium-*B*	212	59·0 11·8 0·13
Radium-*C*	214	0·0424	Thorium-*D*	208	0·035
Radium-*D*	210	16·5 0·36	Radio-actinium ...	—	9·2 0·070
Radium-*E*	210	similar to radium-*D*, but very feeble	Actinium-*B*	—	44·0 11·4 0·165
Mesothorium-*II*..	228	9·5 0·043	Actinium-*D*	—	0·073

Four types may be distinguished in descending order of penetrating power: (1) The known, or old-fashioned, most penetrating type, with μ/d varying from 0·035 to 0·073. The elements long known as γ-ray producers, radium-*C*, thorium-*D*, and actinium-*D* are unique in giving only this single homogeneous type. In addition mesothorium-*II* and radioactinium give a γ-ray of this type, in each case accompanied by another of type (3). (2) Next in penetrating power are some fairly penetrating rays, for which μ/d varies from 0·13 to 0·188 given by the *B*-members only and (4) feeblest in penetrating power of all another set, μ/d 44 to 85, also given only by the *B*-members. There remains to consider (3) a type, with μ/d varying from 9·2 to 16·5, given by all the elements which

[61] A. S. Russell, *Proc. Roy. Soc.*, 1913, A, **88**, 75; *A.*, ii, 270; compare also A. Brommer, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, [iia], 1563.

[62] E. Rutherford and H. Richardson, *Phil. Mag.*, 1913, [vi], **25**, 722; **26**, 324, 937; *A.*, 1913, ii, 461, 901; 1914, ii, 13.

give γ-rays at all, except radium-*C*, thorium-*D*, and actinium-*D*. This type is probably the characteristic *X*-radiation of the respective elements of the *L*-series, type (1) being probably also characteristic *X*-rays of the *K*-series. Type (3) are all less penetrating than hard β-rays and than the *X*-rays of an average tube. Type (4) are of the same order of penetrating power as low-velocity β-rays, and are not greatly superior in this respect to α-rays.

Thorium-*X* also gives a soft γ-radiation, intermediate in penetrating power between the β- and γ-rays of thorium-*D*.[63] If thorium-*C*, which gives the greater and more penetrating part of the β-rays of thorium-*B*+-*C*, gives any γ-radiation at all, it must be of exactly the same penetrating power as that of thorium-*D*. Radium, which, like thorium-*X*, is anomalous in giving some soft β-rays as well as α-rays, has now been found to emit γ-rays also, of intensity about 1 to 1·5 per cent. of that emitted by radium in equilibrium with radium-*B*+-*C*.[64] The radiation appears to consist of three types with μ/d 130, 6, and 0·1.

Further details have been published of the γ-rays excited by the α-rays in elements of high atomic weight,[65] and evidence of such radiation obtained for radiothorium as well as from ionium. Polonium emits a single type of γ-radiation ($\mu/d=215$) due to the polonium itself. When deposited on copper, but not on aluminium, lead, or platinum, a second γ-radiation is present, which is probably the characteristic radiation of copper, in the *L*-series. A very small quantity of β-rays is also emitted from polonium, which could not be ascribed to impurity.

No doubt, when all the details are worked out for the β- and γ-rays, much new light will be thrown on the structure of the atom and the mechanism at work in radioactive processes. A beginning has already been made in the method of studying γ-rays by reflection from crystal surfaces. The γ-rays from radium-*B* ($\mu/d=14·7$) are reflected from a rock salt crystal at angles between 8° and 10°, as a group of fine lines, whereas another series of fine lines were observed reflected at an angle of about 2°, probably resulting from the more penetrating rays of radium-*B* and -*C*.[66]

[63] L. Meitner and O. Hahn, *Physikal. Zeitsch.*, 1913, **14**, 873; *A.*, ii, 906.

[64] A. S. Russell and J. Chadwick, *Phil. Mag.*, 1914, [vi], **27**, 112.

[65] *Ann. Report*, 1912, 300; J. Chadwick, *ibid.*, 1913, [vi], **25**, 193; *A.*, ii, 91; J. Chadwick and A. S. Russell, *Proc. Roy. Soc.*, 1913, A, **88**, 217; *A.*, ii, 372; *Phil. Mag.*, 1914, [vi], **27**, 112.

[66] E. Rutherford and E. N. da C. Andrade, *Nature*, 1913, **92**, 267.

Transmutational Reactions.

There is nothing new to report concerning the question of transmutational reactions produced by the radium emanation.[67] On the other hand, the possibility of a synthesis of helium and neon under the action of the electric discharge has been much discussed. Helium has been obtained from old *X*-ray bulbs, which, after prolonged use, were broken up and heated to redness.[68] The spectrum of the evolved gases, after treatment with cold charcoal, showed the helium lines with great brilliance, and some of the brighter neon lines faintly. In another experiment unopened *X*-ray bulbs were connected by rubber tube to a pump, and, after exhaustion of the connecting tube, communication between the bulb and pump was established by breaking the seal under the rubber. The bulb was heated to 350° and washed out with oxygen, which again showed the presence of helium, and a just detectable trace of neon. On then breaking up these bulbs and heating them, no trace of gas, not absorbed by cold charcoal, was obtained. This makes it appear probable that the helium is in some way produced by the discharge in the tubes, and only loosely held by the glass in a form readily and completely removable by heat.

The work on the production of neon by bombarding fluorite by cathode-rays, referred to briefly last year,[69] has now been published in detail.[70] It was found that neon was obtained, even in absence of fluorite, when the discharge passed in hydrogen. The hydrogen was exploded with excess of oxygen, and treated with cold charcoal. In one experiment the amount of neon was of the order of that obtained in 1 or 2 c.c. of air—that is, of the order of 0·01 cu.mm.—but no nitrogen was found in the gas absorbed by the charcoal. Oxygen and hydrogen put through the pump in the same way as during an experiment, without being submitted to the action of the discharge, gave no neon, neither could it be obtained from the glass and electrodes by heating. From an exhausted bulb, heated in the air to the softening point, no neon was obtained, and to test whether glass subjected to the cathode discharge might be porous to neon, a bulb was completely surrounded by another attached to a separate pump. The cathode-ray discharge was passed through hydrogen in the inner bulb, with the outer bulb exhausted, for two

[67] *Ann. Report*, 1909, 255.

[68] Sir William Ramsay, *T.*, 1913, **103**, 264.

[69] *Ann. Report*, 1912, 308. The reference there given to Sir William Ramsay's letter to *Nature*, in which this result is quoted, is misleading in that it omitted to mention that the author of the work was Prof. Collie, who had not, at the time, published the result himself.

[70] J. N. Collie and H. S. Patterson, *T.*, 1913, **103**, 419.

days, and the usual amount of neon was found in the hydrogen. Now, however, the surprising observation was made that when the outer bulb was washed out with oxygen, a faint explosion on sparking showed the presence of hydrogen, and the residue, after cold charcoal absorption, was about fifty times greater than the residue from the inner tube. This gas was mainly helium with enough neon present to give the spectrum. At this stage the author was joined by H. S. Patterson, who had obtained similar quantities of neon independently, by very similar methods. Pure hydrogen sparked in a Plücker tube and pumped out whilst the discharge was continued showed, after explosion with oxygen and absorption with cold charcoal, the presence of neon, sometimes containing helium, but always with the helium in much greater relative quantity than in the helium-neon mixture obtained by cold charcoal from air. The jacketed tube experiments were also repeated with the same results, and it was found that, when the outer tube contained oxygen, almost pure neon, instead of almost pure helium, was obtained from the gas in the outer vessel.

In continuation of the work,[71] the joint investigators found that electrodes were not necessary for the production of neon, which was formed in hydrogen, free from mercury vapour, submitted to the electrodeless discharge. The jacketed tube experiments were also repeated with the wires connecting the electrodes of the inner tube encased in glass tubes. The apparent disappearance of 3·6 c.c. of hydrogen under the action of the discharge was observed. The gas from the outer tube, examined by filling the latter with mercury and compressing the gas into a spectrum tube, gave a "carbon spectrum." On sparking, it decreased in volume, and the carbon spectrum disappeared. Even after absorption in cold charcoal, which should leave pure helium and neon, this carbon spectrum is seen. The gas causing it appears to be highly uncondensable and not readily oxidised, and it is suggested it may be the "X_3" discovered by Sir J. J. Thomson by his positive ray method. Another observer, with the jacketed tube experiment, found only hydrogen, containing small and varying amounts of carbon monoxide, accumulating in the jacket after discharge in the inner tube. The production of neon from hydrogen sparked in the inner tube ceased after a time, but, on adding a mixture of hydrogen and oxygen and continuing the discharge, the production of neon recommenced.[72] These results have been given fully because it is difficult at the present stage to compress or comment on them. That neon is not always obtained by sparking hydrogen is shown by recent experi-

[71] J. N. Collie and H. S. Patterson, *P.*, 1913, **29**, 217.

[72] J. I. O. Masson, *ibid.*, 233.

ments, of which only the abstract is available at the time of writing.[73] This is in accord with experience of the writer with the calcium method, in which the production of neon from hydrogen under the electric discharge could not fail to have been observed if it were a general phenomenon. There must be some unrecognised factor contributing to the results. In view of the care and circumspection apparently exercised in the performance of the experiments, it would not be fair to conclude that the neon found must necessarily have been of atmospheric origin.

Helium and neon have been commonly found in the positive-ray experiments,[74] but here, where apparently a continuous stream of gas is kept passing through the discharge tube in connexion with a cold charcoal bulb, it must be very difficult to be sure that they are not derived from the atmosphere. In these experiments it was found that the conditions which gave rise to a considerable amount of "X_3" generally gave helium and neon also. The view now most favoured with regard to the nature of "X_3" is that it is probably a modification of hydrogen (H_3). It is obtained by the cathode-ray bombardment of many substances, indeed, most substances, but especially abundantly from potassium salts. The production of hydrogen under the discharge in vacuum tubes is regarded as analogous to the production of "X_3," helium and neon, and the suggestion is made that they may represent abortive attempts at disintegration, analogous to those occurring in radioactive substances, in which the products require the assistance of the cathode-ray bombardment in order to get clear from the atoms producing them.

Chemical and Biochemical Effects of Radioactivity.

A very thorough investigation of the decomposition of water by α-rays has been made. For ice at $-183°$ the products are hydrogen and oxygen in the same proportion as in water, but the amount of decomposition is only a twentieth as great as with liquid water. For the latter, 6·4 per cent. of the energy available is utilised in the decomposition, and the number of molecules of water decomposed is 6 per cent. greater than the number of ions produced by the rays in air. At first hydrogen is produced in excess with formation of hydrogen peroxide. Later there is a disengagement of excess of oxygen. When the rays act on water in the state of vapour, the excess of hydrogen attains 50 per cent. by volume.[75]

These results therefore form an important confirmation of the

[73] Hon. R. J. Strutt, *Proc. Roy. Soc.*, 1914, *A.*, **89**, 499.

[74] Sir J. J. Thomson, *Nature*, 1913, **90**, 645.

[75] W. Duane and O. Scheuer, *Le Radium*, 1913, **10**, 33; *A.*, ii, 270.

view that the number of molecules of liquid water decomposed by the passage of an α-ray is approximately the same as the number of pairs of ions produced by the α-ray in passage through a gas; or, in other words, if the ionisation current in the gas were expressed in faradays, the decomposition in liquid water would be expressed in moles.

Researches on the decomposition of iodides by the penetrating radium rays have been extended to the iodides of the alkaline-earth elements, which show the same general behaviour as those of the alkali metals.[76] Although the effects produced are of a smaller order of magnitude than those observed with ultra-violet light, they are of the same general character. Thus, with ultra-violet light, many organic acids in $N/2$- to $2N$-solution were decomposed, acetic acid to the greatest extent, but with long exposures to the penetrating rays of comparatively large quantities of radium, the effects are excessively minute. Among positive actions of the latter may be mentioned the reduction of silver nitrate solution to metallic silver, the oxidation of ethyl alcohol to acetaldehyde and acetic acid, and the inversion of sterilised aqueous solutions of sucrose.[77] A further study has been made of the action of radium emanation on growing plants.[78] A lasting injury is caused to the plant, whether the exposure is made to the seed or to the seedling, provided that the emanation is of sufficient concentration, and this injury, unlike that caused by tobacco-smoke or coal-gas, continues after the plant has been brought into pure air. In smaller quantities the emanation exerts in some cases a favourable influence. The injury extends not only to the growing parts, but also to the organs already developed, including the leaves. The fall of the leaves is, in certain cases, much accelerated by the emanation, and can be made to occur in spring or summer, when under normal conditions no such tendency exists. Lastly, remarkable changes sometimes occur in the character of the development. The buds of *Sedum Sieboldii*, instead of developing normally into trefoliated whorls, after exposure, in a quite early stage of growth, to strong emanation for three days, develop with decussate pairs of leaves. In some ways the action of the emanation resembles that of a poison, but there is probably no poison known capable of producing such great effects in such infinitesimal quantity.

[76] *Ann. Report*, 1912, 323.

[77] A. Kailan, *Monatsh.*, 1913, **34**, 359, 1209, 1245, 1269; *A.*, ii, 270, 1000, 1002, 1003.

[78] H. Molisch, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, [iia], 833.

The Penetrating Radiation of the Atmosphere.

In seven balloon ascents in 1912 measurements of the ionisation in a closed electroscope were carried out, and the results show that there is a very small decrease of the penetrating radiation between 200 and 1000 metres, and then an increase, so that at heights from 1000 to 2000 metres the radiation has much the same value as at the surface. In one ascent, in which a height of 5350 metres was attained, a very considerable increase of the radiation was observed above 3000 metres, and the increase became very marked at the greatest height attained. This increase above 3000 metres was independently confirmed, and in 1913 in another voyage, in which 4160 metres was attained, the same slow increase from 2000 to 3500 metres and rapid increase at the highest level was observed, although the weather conditions were quite different from that of the earlier ascents. The conclusion is drawn from this that a very penetrating radiation must enter the upper atmosphere from outside space, and cause part of the spontaneous ionisation in closed vessels observed at the surface. This part is probably that for which large and irregular variations have been noticed, but as no diminution was observed in the ascents at night and during a solar eclipse, the source of this radiation can scarcely be the sun. It is estimated that only one-twentieth part of the penetrating radiation observed at 1000 to 2000 metres height can be due to the radium-*C* in the atmosphere, assuming that this is no greater than at the surface. At this height the rays from the earth's surface would be so much absorbed by the air as to be negligible. The conclusion is a somewhat sensational one. When it is considered that the atmosphere is equivalent to 76 cm. of mercury, and would reduce the γ-radiation of radium to between 10^{-19} and 10^{-20} of the initial value, the assumption of an external radiation reaching the surface of the earth from outer space would seem to involve the existence either of more penetrating rays than are yet known, or of cosmical sources of radioactivity of unparalleled intensity.[79]

FREDERICK SODDY.

[79] V. F. Hess, *Sitzungsber. K. Akad. Wiss Wien*, 1912, **121**, [iia], 2001 ; 1913, **122**, [iia], 1053, 1481.

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136	16	*for* "benzoyl-*p*-phenylenediamine" *read* "benzoyl-*o*-phenylenediamine."

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